Table of contents

TABLE OF CONTENTS 1

1. PRINCIPLES OF OPERATION 5

1.1 PREFACE 5
1.2 THE CONCEPT 6

2. GETTING STARTED WITH GPES 9

2.1 RECORDING A CYCLIC VOLTAMMOGRAM WITH THE DUMMY CELL 10
2.2 THE USE OF THE MANUAL CONTROL WINDOW 13
2.3 DATA MANIPULATION OF A CYCLIC VOLTAMMOGRAM. 14
2.4 CALCULATION OF A CORROSION RATE. 17
2.5 NOISE REDUCTION 19
2.6 DATA ANALYSIS WITH CHRONO-AMPEROMETRY. 20
2.7 DATA ANALYSIS WITH DIFFERENTIAL PULSE VOLTAMMETRY. 21
2.8 ANALYSIS OF ELECTRO CHEMICAL NOISE 22
2.9 IR-COMPENSATION 23
2.10 DETECTION OF NOISE PROBLEMS 24

3. THE GPES WINDOWS 27

3.1 GPES MANAGER WINDOW 27
File menu 27
Method 32
Utilities 32
Project 43
Options 51
Window 52
Help 52
Tool bar 52
3.2 STATUS BAR 53
3.3 MANUAL CONTROL WINDOW 53
Current range 54
Settings 54
Potential 55
Noise meters 55
iR-compensation 55
Integrator 56
Filter panel 56
3.4 DATA PRESENTATION WINDOW 56
File 57
Copy 58
Plot 58
Analysis 60
Edit data 60
Work scan 60
Work potential 60
Editing graphical items and viewing data 60
3.5 EDIT PROCEDURE WINDOW 63
3.6 ANALYSIS RESULTS WINDOW 64

4. ANALYSIS OF MEASURED DATA 65

4.1 PEAK SEARCH 65
4.2 CHRONOAMPEROMETRIC PLOT 69
4.3 CHRONOCOULOMETRIC PLOT 69
4.4 LINEAR REGRESSION 69
4.5 INTEGRATE BETWEEN MARKERS 70

4.6 WAVE LOG ANALYSIS 70
4.7 TAFEL SLOPE ANALYSIS 71
4.8 CORROSION RATE 71
4.9 SPECTRAL NOISE ANALYSIS 73
4.10 FIND MINIMUM AND MAXIMUM 74
4.11 INTERPOLATE 74
4.12 TRANSITION TIME ANALYSIS 74
4.13 FIT AND SIMULATION 74
The simulation method *75*
The fitting method *75*
Elements of the Fit and Simulation Window *76*
Fitting and simulation step by step *76*
Fitting in more detail *81*
Fit and simulation error messages *84*
Descriptions of the models *85*
4.14 CURRENT DENSITY 95
4.15 WE2 VERSUS WE PLOT 95
4.16 ENDPOINT COULOMETRIC TITRATION 95

5. EDITING OF MEASURED DATA 97

5.1 SMOOTH 97
5.2 CHANGE ALL POINTS 98
5.3 DELETE POINTS 98
5.4 BASELINE CORRECTION 98
5.5 SUBTRACT DISK FILE 99
5.6 SUBTRACTION OF SECOND SIGNAL FROM FIRST SIGNAL. 99
5.7 DERIVATIVE 99
5.8 INTEGRATE 99
5.9 FOURIER TRANSFORM 100
5.10 CONVOLUTION TECHNIQUES 100
Detection of overlapping peaks *102*
Determination of formal potential and the number of electrons involved *104*
Irreversible homogeneous reaction consuming the product of the electrode process *105*
Investigations of factors controlling the transport to the electrode *106*
Algorithms for convolution *108*
5.11 CONVOLUTION IN PRACTICE 109
5.12 iR DROP CORRECTION 110

APPENDIX I GPES DATA FILES 111

APPENDIX II DEFINITION OF PROCEDURE PARAMETERS 113

APPENDIX III COMBINATION OF GPES AND FRA 127

APPENDIX IV MULTICHANNEL CONTROL 129

Installation and test *129*
Program operation *130*

APPENDIX V TECHNICAL SPECIFICATIONS 133

Interface for mercury electrodes (IME 303 and IME663) *134*
Burettes *134*
Hardware specifications of optional modules *134*
SCAN-GEN, SCAN250: analog scan generator module *134*
ADC750: dual channel fast ADC module *135*
ECD: low current amplifier module *135*
BIPOT, ARRAY and BA: (bipotentiostat) module *135*
FI20: filter and integrator module *135*
BSTR10A or Booster20A: current booster *135*

INDEX 137

1. Principles of operation

1.1 Preface

Autolab and the General Purpose Electrochemical System software (GPES) provide a fully computer controlled electrochemical measurement system.

It can be used for different purposes, i.e.:
- general electrochemical research
- polarographic analysis in conjunction with a dropping or static mercury drop electrode
- voltammetric analysis with solid electrodes, such as glassy carbon or rotating disk electrodes
- research of electrochemical processes like plating, deposition and etching
- electrochemical corrosion measurements
- electrochemical detection in Flow Injection Analysis (FIA) and High Performance Liquid Chromatography (HPLC).

The instrument is controlled by a personal computer equipped with an IBM/PC or AT I/O expansion bus. All the Autolab configurations are supported by GPES:
- µAutolab or µAutolab Type II, the compact version of a standard Autolab with potentiostat
- Autolab with potentiostat/galvanostat PGSTAT10/12/20/30/100 and other, optional, modules.

The GPES combines the measurement of data and its subsequent analysis. GPES runs under MS-Windows 95, 98 and NT. Its installation is described in the "Installation and Diagnostics" guide.
The user should be familiar with MS-Windows.
The GPES program consists of two distinct parts i.e.:
- The user-interface, graphics and data-analysis software.
- The routines which perform all the communication with the Autolab instrument.

Both parts communicate via shared memory. The measurement tasks run with the highest priority. All the spare time is left for MS-Windows applications.

Familiarisation with GPES is best obtained by experimenting. Most of the required help which might be necessary to perform the measurements and the data analysis is provided for by the on-line help within the program.

This manual concentrates more on explaining the general concepts and backgrounds than on guiding the user through the program. Moreover, this manual tries to explain the possibilities of GPES. The "Installation and Diagnostics" guide explains the hardware aspects, the computer requirements and the installation.

1.2 The concept

The design of GPES Windows has been based on the following ideas:

- GPES should incorporate the facilities electrochemists need.
- The user should have full and easy control over the Autolab instrument via the computer.
- 'How to perform experiments' should be easy and clear.
- Actions should require only a few clicks.
- The introduction learning period should be short.
- All important electrochemical techniques should be available.
- GPES should be a full and standard Windows application.
- Series of unattended experiments, using different techniques and/or procedures, should be possible.

The GPES screen consists of several windows: one for manual control over the potentiostat/galvanostat, one for data presentation and manipulation, one for entering the experiment parameters and one for collecting results of data analysis. Surrounding windows, menu options and tool bars give extra facilities like cell-diagnosis, accessory control, Autolab configuration, access and data transfer to programs like Excel and MS-Word.

The MS-Windows related terminology used in this manual is in agreement with the standard as described in the book "The GUI Guide - international terminology for Windows Interface" (Microsoft Press, Washington ISBN 1-55615-538-7). It is a good book to become acquainted with the Windows vocabulary.

The following mouse conventions are used:

- Quickly pressing and releasing the mouse button is called "clicking". A click of the left mouse button on a menu option, a button, an input item on the screen, etceteras will result in an action.
- Clicking and holding down the left mouse button is called "dragging" and is used for several purposes. You can focus on an item on the screen without an action, you can drag a window when the mouse pointer is in its title bar. It can be used to shrink or to enlarge a window when the mouse pointer is on the border of a window. Finally, you can drag a scroll bar, a slider or a zoom-panel.
- A double-click of the left mouse button is used to perform particular actions. Except for the standard uses in window actions, it is used to edit the graph in the Data presentation window.
- A click of the right mouse button is used to open a zoom panel in the Data presentation window or to shrink or enlarge the Graphics panel in the Setup Template option in the Print menu window, which appears after selecting Print from the File option in the GPES Manager window.

The following keyboard functions are supported:

- RETURN/ENTER key:
  jump to next data input field;
  select menu option; or
  click button with focus.
- left and right arrow key:
  move cursor in data input field.
- up and down arrow:
  move up and down in potential/current level input in chronomethods; or
  move up and down in a menu.
- ALT:
  puts focus on the menu bar of the window with the focus;
  typing a subsequent underlined character will move the cursor to the corresponding menu item, a RETURN/ENTER will select the menu item.
- ESC: aborts the execution of the measurement procedure.
- F1: access Help.
- F4: plot rescale.
- F5: starts the execution of the measurement procedure.
- F6 and shift F6: change focus to the next window.

This manual does not describe the background of the electrochemical methods. We would like to refer to the ‘Electrochemical methods’-manual and some excellent textbooks:

- C.M.A. Brett and A.M.O. Oliveira Brett,
  Electrochemistry
  Oxford science publications ISBN 0-19-855388-9

- Allen J. Bard and Larry R. Faulkner,
  Electrochemical Methods: Fundamentals and Applications
  J. Wiley & Sons ISBN 0-471-05542-5

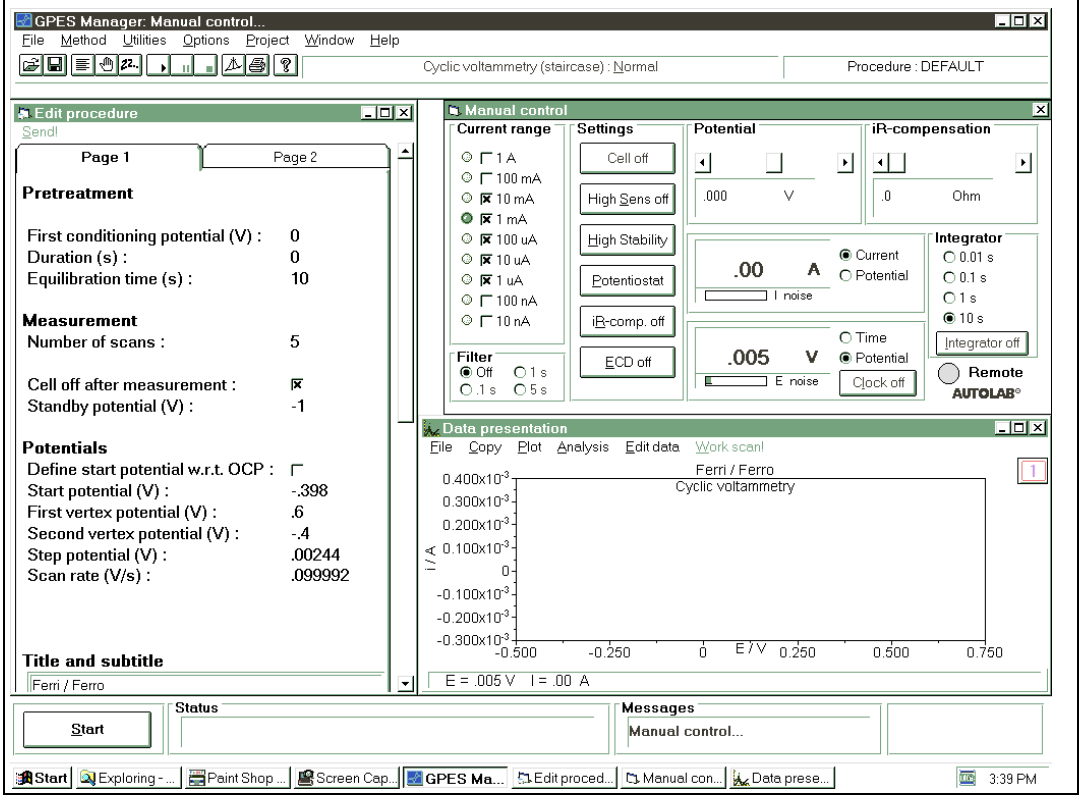
- R. Greef, R. Peat, L.M. Peter, D. Pletcher and J. Robinson,
  Instrumental Methods in Electrochemistry
  Ellis Horwood Limited ISBN 0-13-472093-8.

2. Getting started with GPES

In this chapter some basic examples are given to become familiar with GPES. The possibilities and the options of the software are described. Some of the examples contain a measurement with the Autolab dummy cell, so before you start with the first example, please connect the dummy cell box to the cell cable by putting the banana plug connector into the matching colour connector on the dummy cell. The red banana plug should be connected to WE(a).

As soon as you start GPES, by clicking the icon in the Autolab application window, you will see the standard layout of the GPES software, which consists of three windows and two bars.

Fig. 1 *Default layout of GPES windows*



The two bars are:

- The GPES manager bar, with the menus and the tool buttons.
- The Status bar at the bottom of the screen, which contains the start and stop buttons for measurement and displays the system messages.

The three windows are:

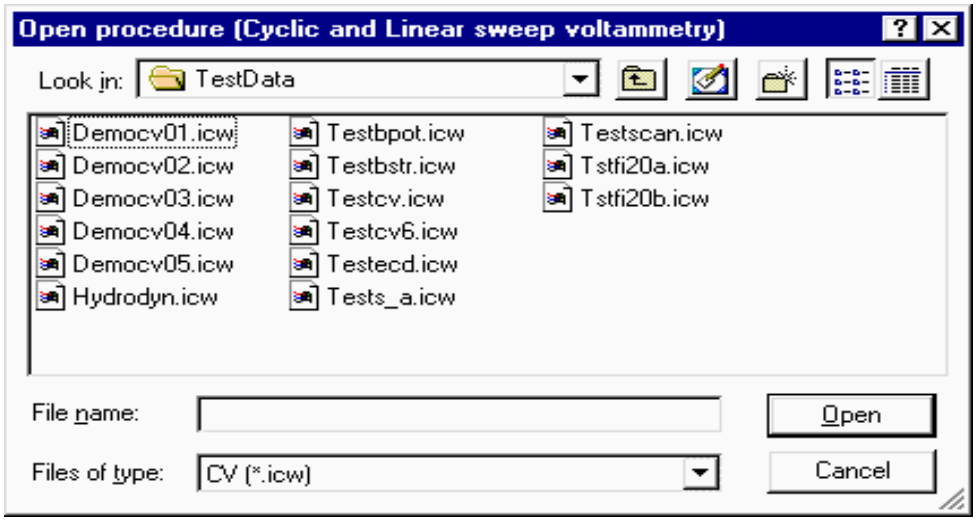
- The Edit procedure window, which specifies all the experimental parameters. Changed parameters are automatically saved when leaving the software and will appear as default parameters on the next occasion. For most of the techniques, this window will consist of two pages.
- The Manual control window, which manually controls the settings of the potentiostat/galvanostat.
- The Data presentation window, which gives a graphical display of the measured data, and allows you to do data analysis and/or modification.

The options and possibilities of these three windows will be explained in detail in the next chapter.

2.1 Recording a cyclic voltammogram with the dummy cell

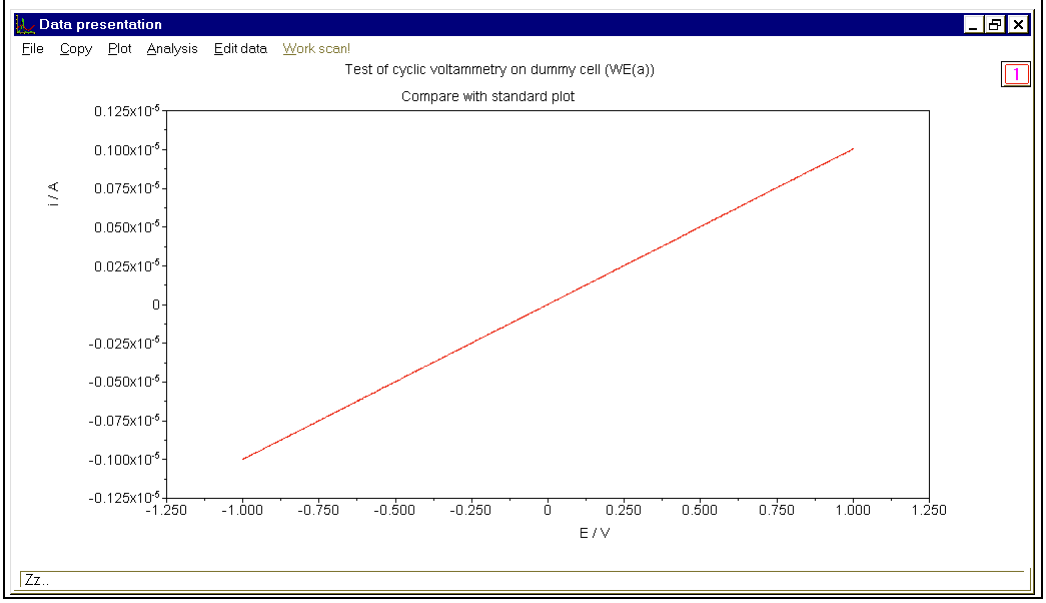
1. Before starting with this (and with the other examples) please check the hardware configuration of your system. You can do this by executing the hardware configuration program. In the Autolab hardware configuration window, you can check if all the modules in your instrument are also selected in the software, if so, you can close this window by clicking 'OK'. See also the Installation and diagnostics manual.
2. From the Method menu of the GPES manager bar, please select 'Cyclic voltammetry (staircase) Normal'.
3. Select 'Open procedure' from the File menu, and open the 'testcv.icw' from the \autolab\testdata directory.

Fig. 2 *The Open procedure window*



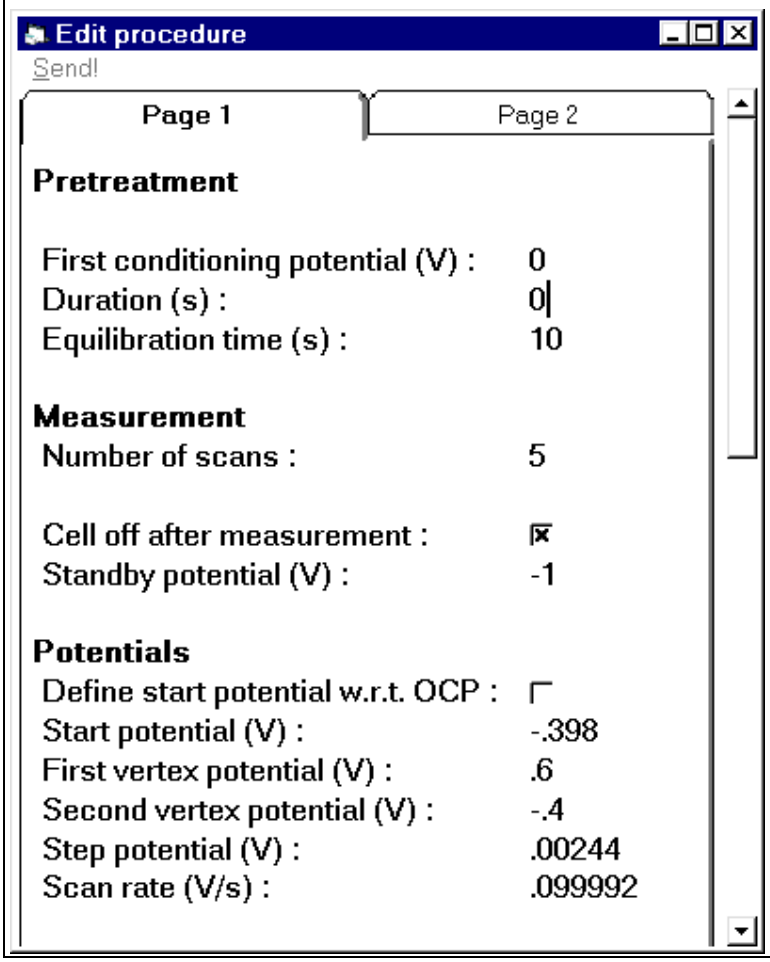
4. In the Edit procedure window, you will now find all the measurement parameters. By clicking ‘Start’ the program will start the dummy cell measurement. During the measurement you can automatically rescale the curve in the Data presentation window by typing F4 on your keyboard.

Fig. 3 *Results of procedure TESTCV*



5. After the measurement is done, the curve should look like the curve in figure ‘Results of procedure TESTCV’, i.e. a straight line, if not, please consult the “Installation and Diagnostics” guide in this manual.
6. In the Edit procedure window, please select ‘Number of scans’ and change the value from 1 to 100. If you now press start again, the program will start to do 100 scans. You can always stop the measurement by using ‘Esc’ on your keyboard, or by clicking the Abort button. Please do so after a few scans. After stopping, the Data presentation window will show you the last scan. You can also select one of the previous scans by using the Work scan option.
7. You are able to change some measurement parameters during the measurement by using the Send option in the Edit procedure window. Please (re)start a measurement with 100 scans and during the measurement change the ‘Scan rate’ from 0.1 V/s to 1 V/s. After clicking ‘Send’ the speed of the measurement will increase. You can again stop the measurement by using the ‘Esc’ button.

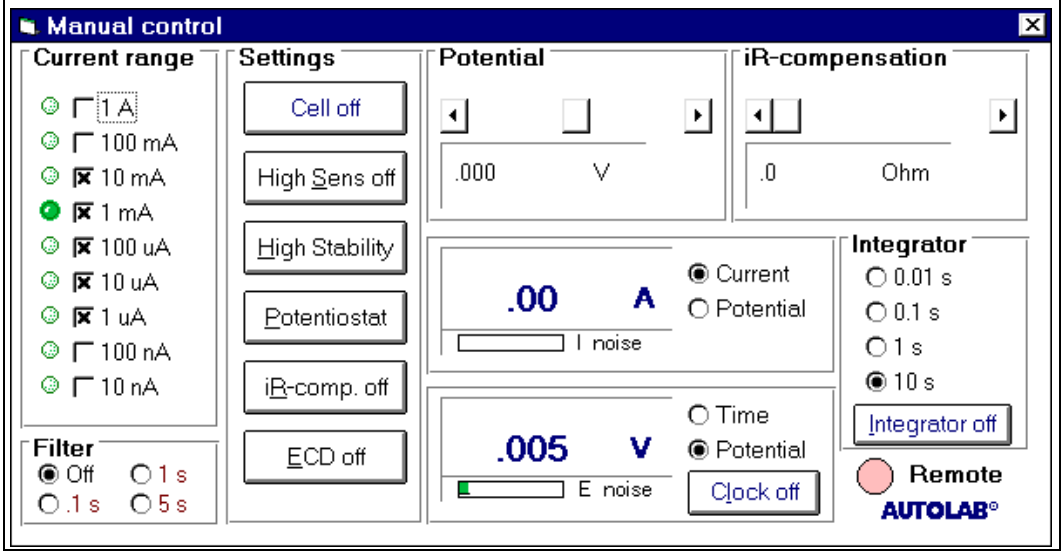
Fig. 4 *Edit procedure window*



8. After finishing a measurement, the program allows you to save more than one scan by selecting ‘Save scan’ and then selecting a scan that you would like to save. For the following scans you want to save, please select ‘Save scan as’. The ‘Save data buffer’ option saves all the scans that the PC has in its memory.

2.2 The use of the Manual control window

Fig. 5 *Manual control window: the appearance depends on the Autolab configuration*



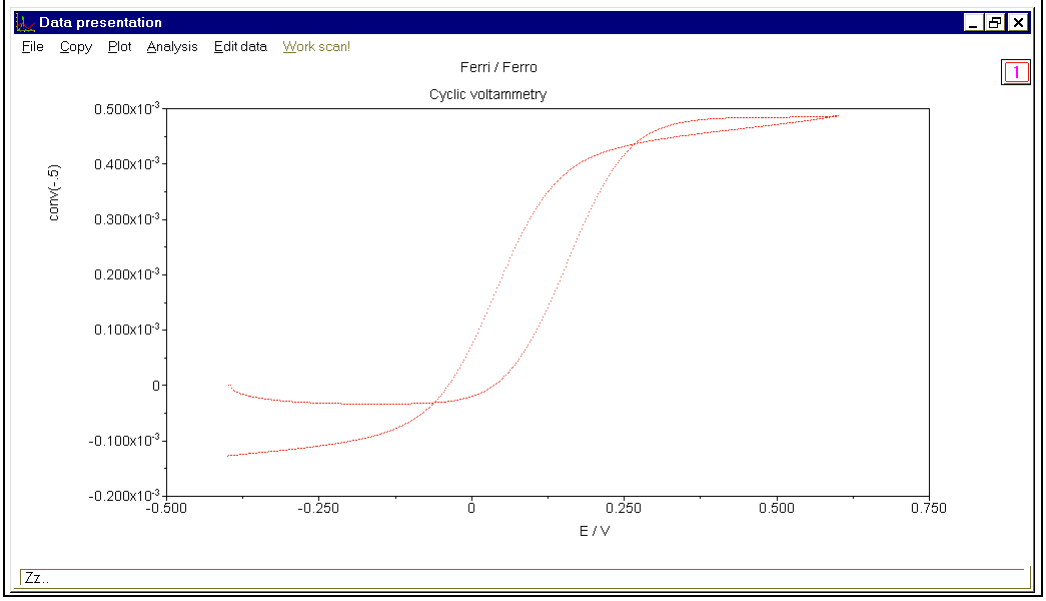
The Manual control window allows you to control the potentiostat manually, instead of via a measurement procedure. With the dummy cell still connected to the cell cable, and the procedure “testcv” loaded, you can try the following:

1. Clicking the highest current range (10 mA for a PGSTAT10/µAutolab, 100 mA for a PGSTAT12/100 and 1 A for a PGSTAT20/30) results in the selection of all current ranges except the 100nA range. This allows automatic current ranging using all the ‘checked’ ranges, during the execution of a measurement procedure. The green circle indicates which current range is active. Check this by clicking on one of the circles and see what happens on the front panel of the potentiostat.
2. The cell can be switched on and off manually, please click the cell on/off button, and check the result on the potentiostat.
3. By using the slider below ‘Potential’ it is possible to set a potential value. Make sure that the cell is ‘on’ and use the slider to set a potential of 1 V. In the Manual control window the current and the potential are given. By clicking the Clock on/off button the program will start making a graph of the current versus time. Switch the clock off again, and use the window below the slider to set a potential of 0 V. Switch the cell off again.

2.3 Data manipulation of a cyclic voltammogram.

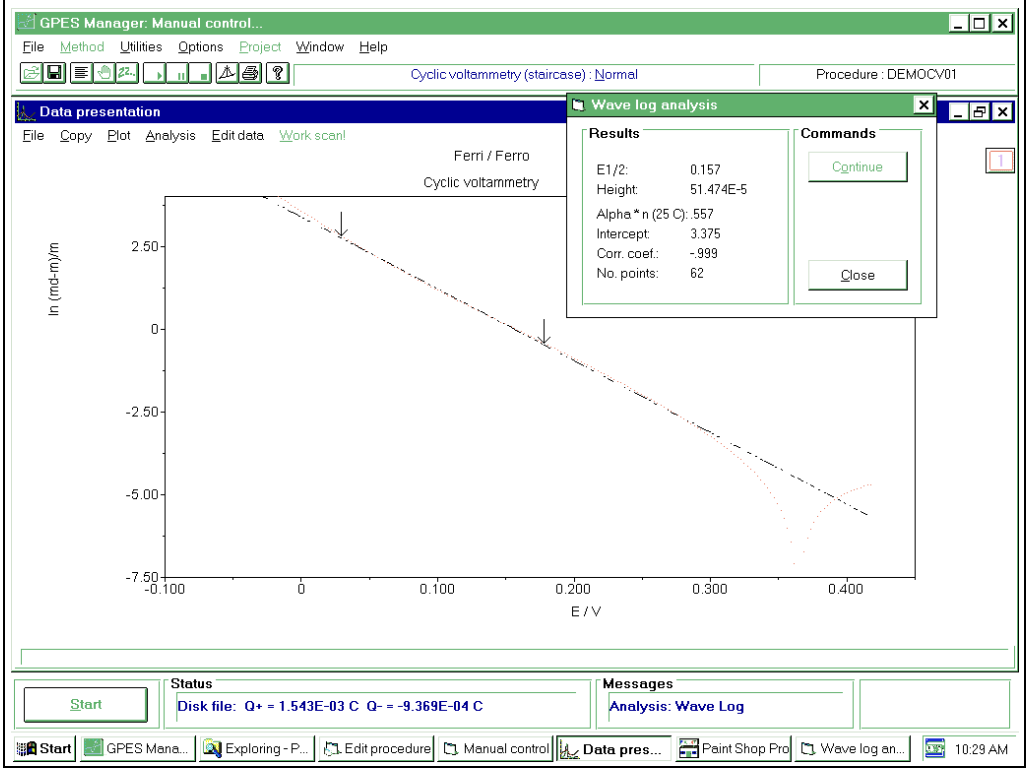
1. Choose ‘File’ and ‘Load scan’ and load the datafile ‘democv01’ in the \autolab\testdata directory. Enlarge the graph by clicking the maximise button on the Data presentation window.
2. Double click the curve in the Data presentation window. A plot parameter window appears, in which you can change the colour of the curve, or change from a ‘line’ display to a ‘scattered’ display.
Please try this by changing the colour and the style of the line. Select the settings that you feel are the most suitable for this curve.
3. With the peak search option, the software allows you to determine all peak parameters of the CV. Choose ‘Analysis’ and ‘Peak search’. When the Peak search window appears, click the Options>> button, the program now allows you to set a number of options. Start by selecting ‘Curve cursor’ and ‘Lin. front baseline’, click close and press the search button in the Peak search window. You are now asked to set two markers for a baseline in front of the peak, please do so and press OK. The program shows the result of the peak search in the ‘Peak search results window’ and shows the peak in the curve.
4. Please repeat the above after selecting ‘Automatic’ and ‘Linear baseline’ in the Options>> window. Click search, and have a look at the results.
5. Close the Peak search results window and choose ‘Window’ and ‘Analysis results’ from the GPES manager bar. In this window all the data analysis results are kept as long as you do not exit the GPES software. Please check under ‘File’ that you are able to ‘Save’, ‘Print’ or ‘Clear’ the results. Close the Analysis results window.
6. Under ‘Edit data’ choose the option ‘Subtract disk file’. Select the same file that has been loaded: ‘democv01’. Note that, as might be expected, the result is a horizontal line at I=0. By selecting ‘Plot’ and ‘Resume’ the original curve is retrieved. This option always allows you to get back to the original curve after editing or analysing the data.
7. Under ‘Edit data’ choose the option ‘Baseline correction’. Select ‘Linear baseline’ at the settings, and press ‘Set markers’. You are now asked to set two markers for the baseline you want to correct. Set the markers on the horizontal part of the forward curve before the peak and press ‘OK’. Note that the Data presentation window now shows you both the original and the corrected curve (in black). By clicking OK you accept the corrected curve and the original is removed from the window. Using the ‘Resume’ option, however, gives you back the original.
8. The option ‘Wave Log analysis’ under ‘Analysis’ allows you to determine the half-wave potential and the number of electrons for S-shaped voltammogram, for example a Normal pulse voltammogram. The file ‘democv01’ may be transferred to an S-shaped curve by choosing ‘Edit data’, ‘Convolution’ and ‘Time semi-integral’. For more details on the convolution techniques, please read the relevant chapter in this manual.

Fig. 6 *Results of time semi-integral convolution*



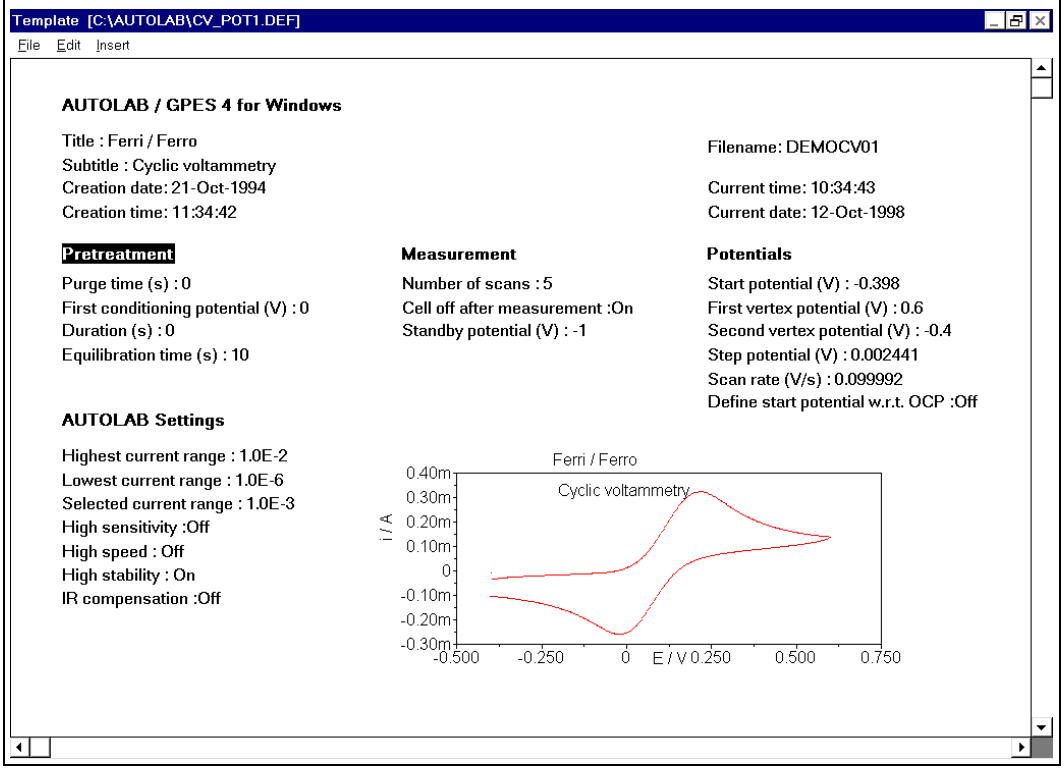
After selecting ‘Wave log analysis’, you are asked to set markers for the baseline and the limiting current line for the forward (or black) curve. Please set two markers for the baseline and press OK and do the same for the limiting line. Now the Wave log analysis window gives you a value for the half-wave potential and the height of the curve. By clicking ‘Continue’ the curve transforms and you are again asked to set two markers. After doing this and clicking OK, you get the results for the analysis in the Wave log analysis window.
Close this window and choose ‘Plot’ and ‘Resume’.

Fig. 7 *Wave log analysis option*



9. From the GPES manager bar, choose ‘File’ and ‘Print’, the Print menu allows you to print the measured data, one or more of the windows, and a Template. Select ‘Template’ and ‘Set-up template’. With this option you can print a measured curve together with the most important measurement parameters on one sheet. With ‘Insert’ and ‘Field’ you can add or remove fields with parameters from the template. You can also drag fields around to put them on another place on the sheet. By clicking ‘File’ and ‘Print preview’ the values for the parameters and the curve are shown. The size of the curve may be changed by clicking it with the right mouse button and then moving your mouse (without pressing a button!). The way in which the parameters are displayed may be changed by double clicking a field and choosing for example ‘scientific’ and then setting a precision. (Precision -1, means that the value is printed with the format used in the Edit procedure window). Close the Template window.

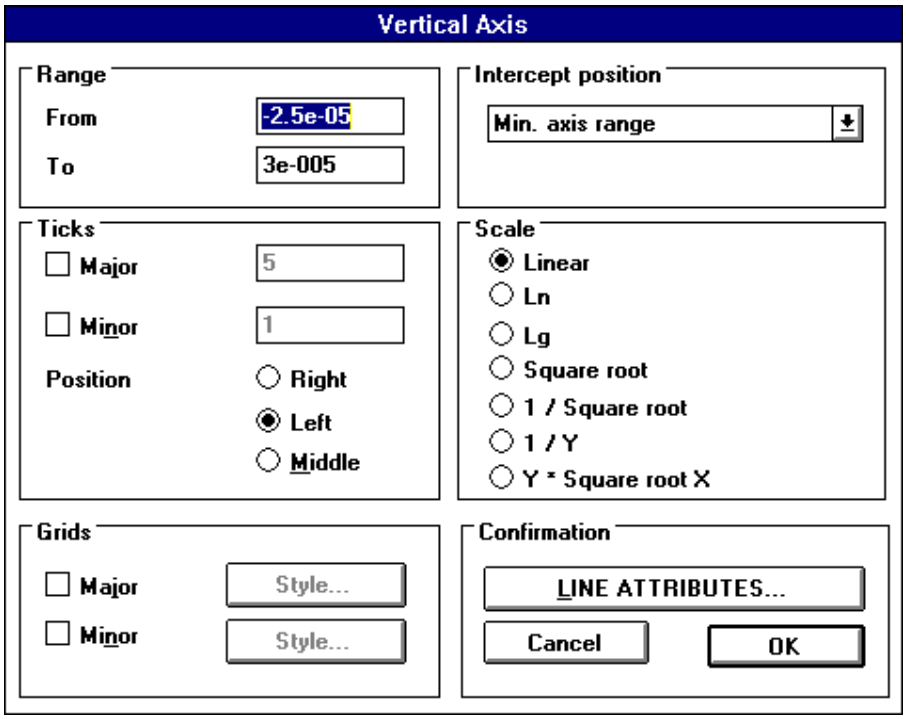
Fig. 8 *Results of printing of the template*



2.4 Calculation of a corrosion rate.

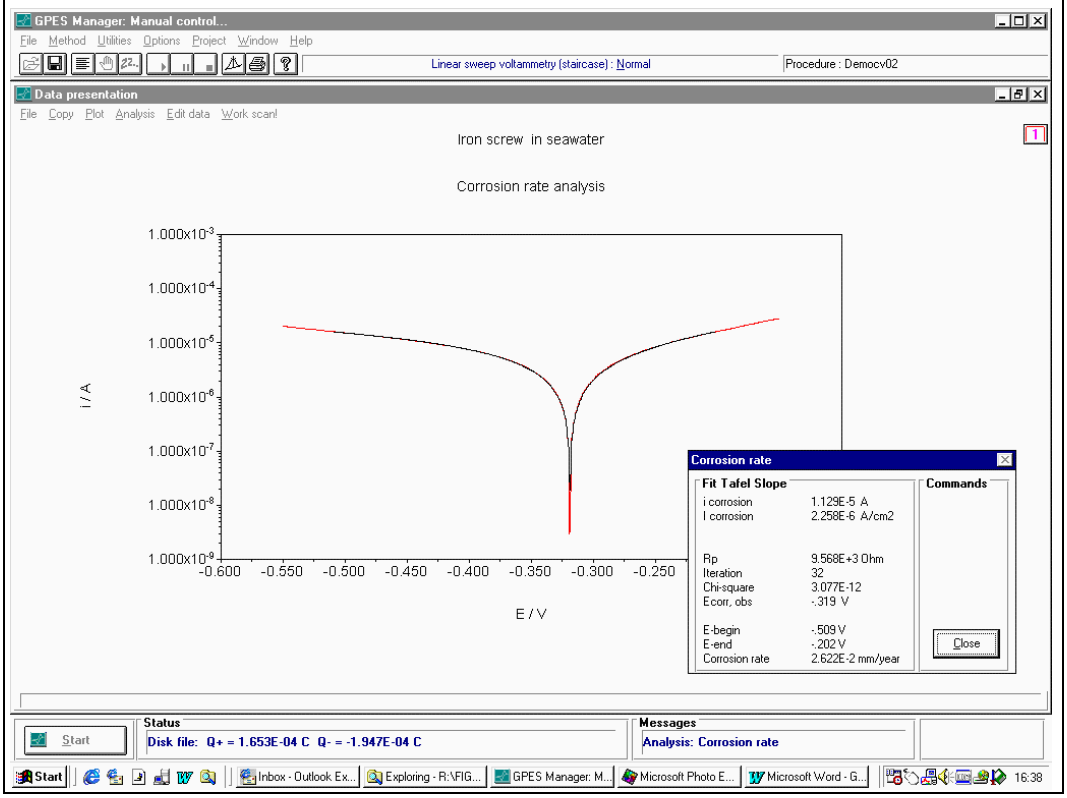
Before you start, make sure that the method is still Cyclic Voltammetry, Normal.
1. Load the datafile ‘democv02’ from the \autolab\testdata directory.
2. In the Data presentation window, double click the vertical axis. The vertical axis window appears.

Fig. 8a *Vertical axis window*



3. Change the scale from the axis from linear to Lg, i.e. 10log. Please note that you are also able to change the range of the axis and the position of the intercept of the axis in this window. Close the window, and note the change of the curve.
4. From the Analysis menu, choose ‘Corrosion rate’. The Corrosion rate window appears.

Fig. 9 *Corrosion rate analysis*



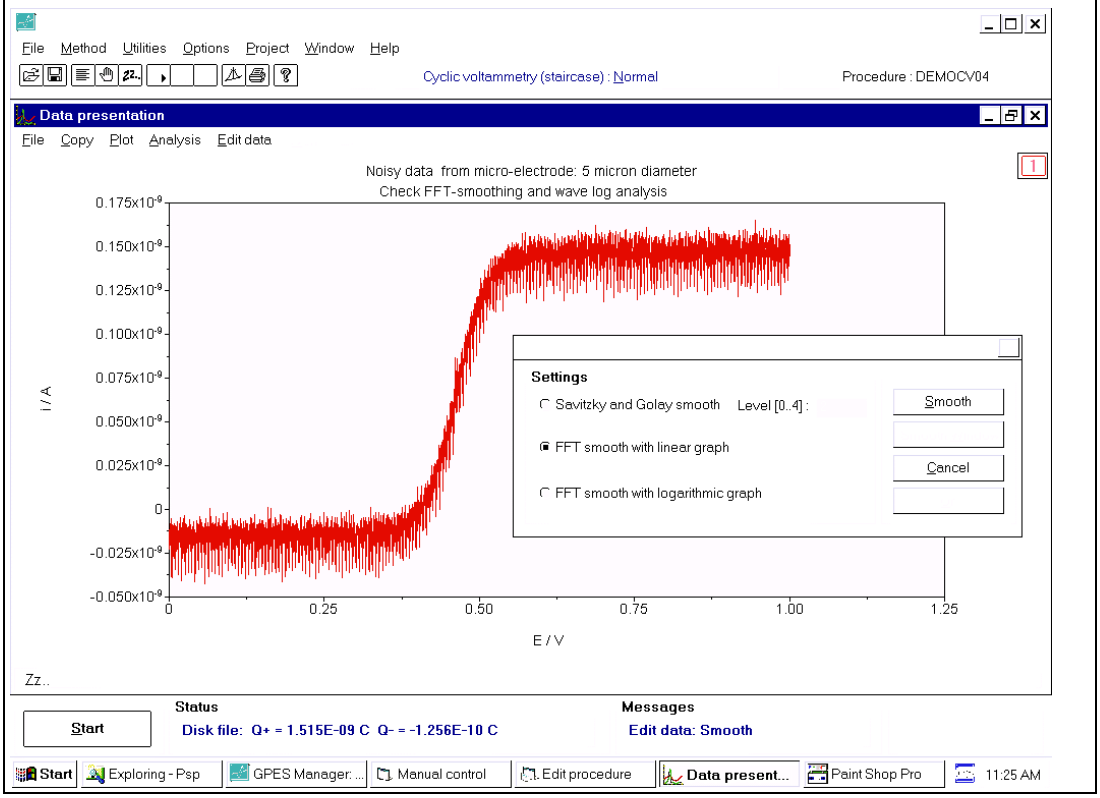
In this window the program shows a first value for the corrosion potential, as well as for the polarisation resistance. Furthermore you can specify values for the surface area, the equivalent weight and the density of the material you are using. For this example you can set these values to 1. Click the Tafel slopes button. You are asked to set markers on the anodic branch and on the cathodic branch. After you have done so, the Corrosion rate window appears, with a list of parameters, among which the corrosion rate in mm/year. By clicking the Start fit button, the software will adjust the parameters until a best fit of the original curve is found. This fitted curve is shown in black, and the final values for the parameters are given.
Click close and transform the vertical axis of the curve back to linear.

2.5 Noise reduction

Make sure that the method is Cyclic voltammetry (staircase), normal.
1. Load the datafile ‘democv04’ from the \autolab\testdata directory.
2. From the Edit data menu, choose the Smooth option. The Smooth window appears, and gives you the possibility to choose from different smoothing methods. Choose FFT (Fast Fourier Transform) with linear graph. Click the Smooth button, the curve is now transformed to the frequency spectrum and a marker window appears. You are asked to set one marker for the cut-off frequency: set this marker at ca 7 Hz and press

OK. All frequencies above 7 Hz will now be filtered out. Please note that the 7 Hz is not the frequency of the potential or current noise. The scaling is arbitrary. Note the smoothed curve in black, with OK you accept the curve, and the noisy original will disappear.

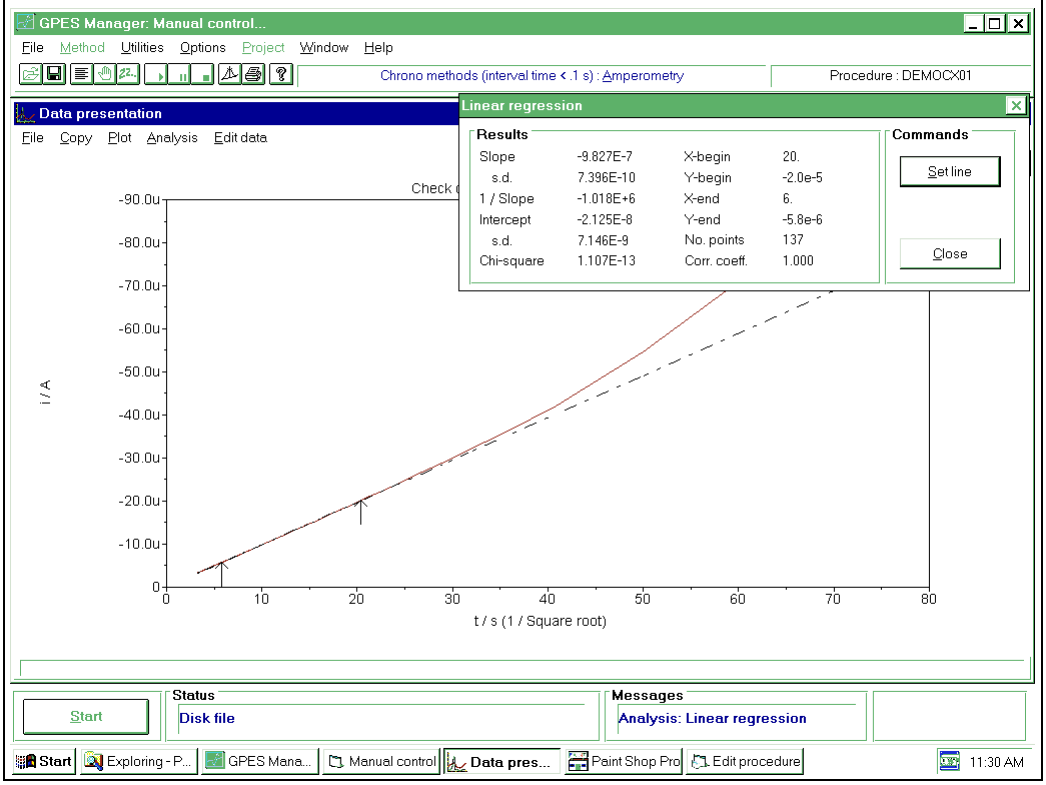
Fig. 10 *Data smoothing using FFT*



2.6 Data analysis with Chrono-amperometry.

From the Method menu on the GPES manager bar, choose Chrono-amperometry (interval time < 0.1 s).
1. Load the datafile ‘democx01’ from the \autolab\testdata directory.
2. The curve shown is the result of a double potential step experiment. To do data analysis it is more convenient to choose just one of both potential levels at a time. To do so, from the Plot menu in the Data presentation window, choose select potential, and select the -0.7 V level. The data shown now are the result of the selected potential step.
3. In Chrono-amperometry the current is proportional to 1/Square root of time. In order to visualise this, please double click the horizontal axis and change the scale to 1/square root. The curve is now linear. From the Analysis menu, choose ‘Linear regression’ and set two markers for the beginning and the end of the linear regression. The Linear regression window now gives you the results. From the slope of this line, it is possible to calculate for example the diffusion coefficient.

Fig. 11 *Transition time analysis*



4. From the Plot menu choose ‘Resume’ and the original curve will reappear.

2.7 Data analysis with differential pulse voltammetry.

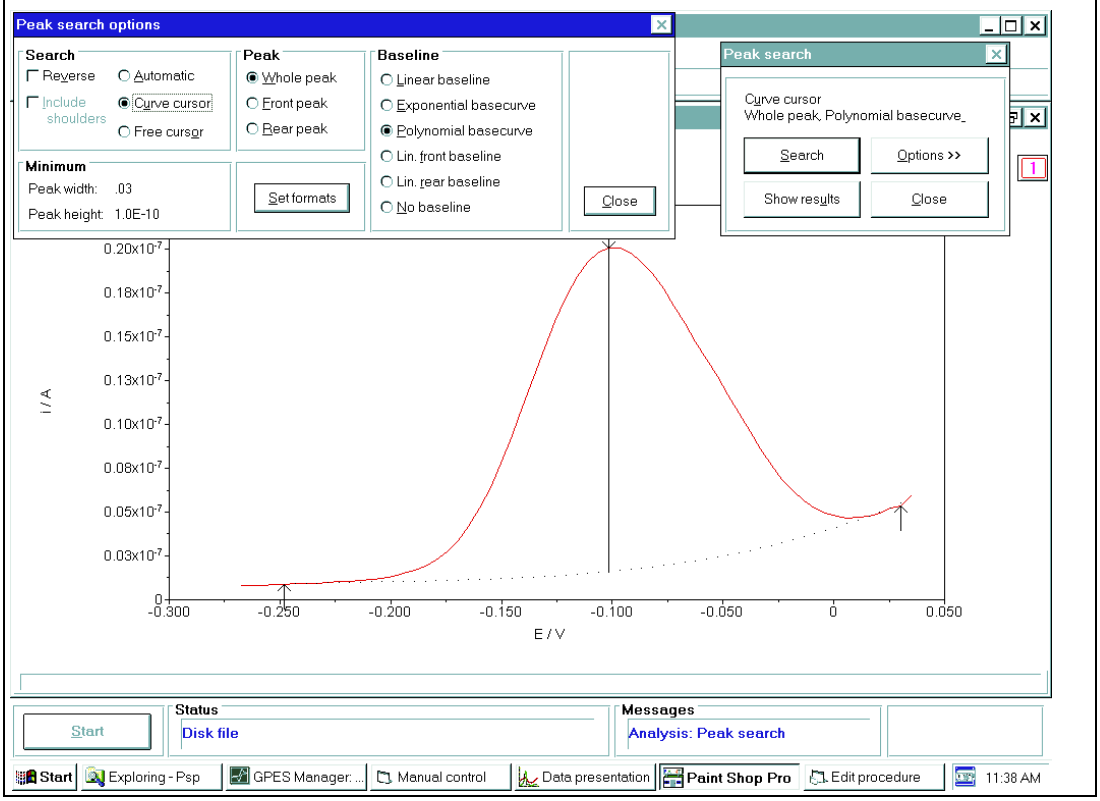
From the Method menu, choose voltammetric analysis and then Differential Pulse.
1. Load the datafile ‘demoea01’ from the \autolab\testdata directory.
2. From the Analysis menu choose Peak Search. Under the options, choose the automatic search, close the Options window and press the search button. The Peak search results window will now show parameters for four peaks. For the first three the results are reasonable, but for the peak at the highest potential the linear baseline is not the best option.
3. With the Set window option under the Plot menu, you are able to extract the last peak from the curve. Set the markers so that only the last peak is visible. Now there are two options (please start each option after setting the window around the last peak):

a. From the Edit data menu choose ‘baseline correction’ and select the polynomial basecurve. Click the set markers button and set the markers for the baseline (one on each side of the peak). After ‘OK’, the corrected (black) curve is shown with a more horizontal baseline. You can now use the automatic peak search option to find the

peak parameters. Please do so and check the difference with the automatic search on the non-corrected curve by opening the Analysis results window.

b. From the Analysis menu, choose the Peak search option. Under options, choose ‘curve cursor’ with a polynomial baseline. After pressing the Search button you are asked to set two markers for the baseline, please do so. Now the Peak search results window will give you the parameters of this search. Please open the Analysis results window to compare this option with the result of option a. As should be expected, the results of these two options are very similar. Close the Analysis results window.

Fig. 12 *Example of polynomial baseline correction*

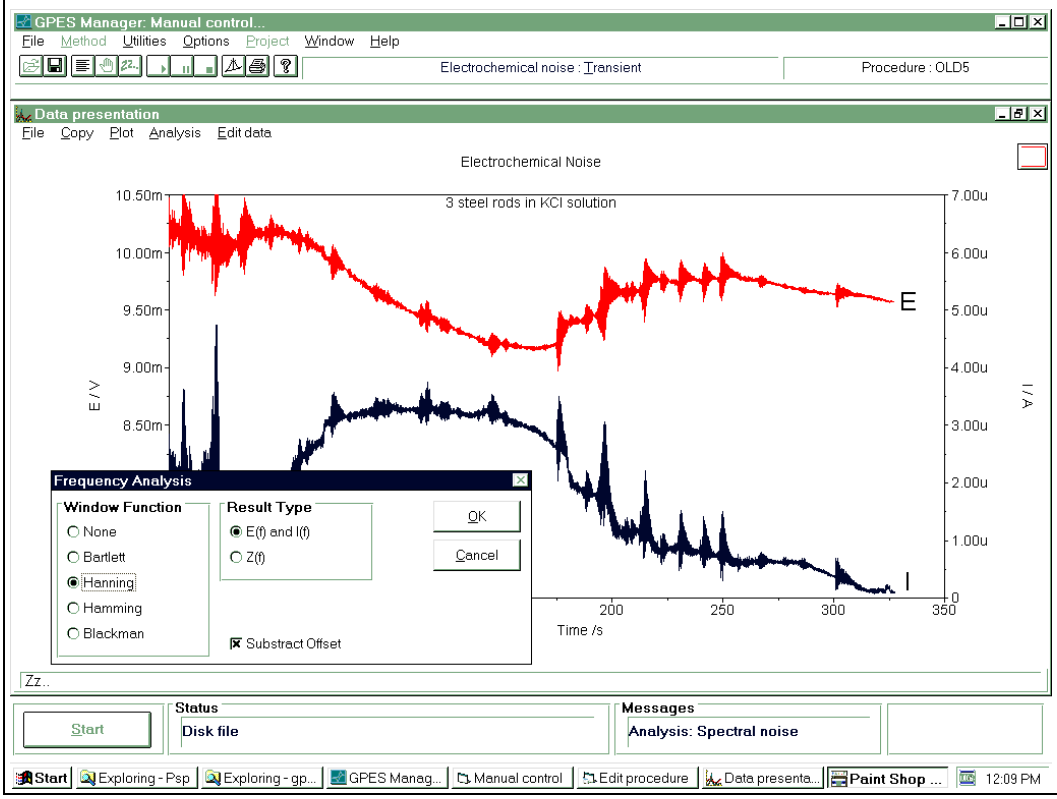


2.8 Analysis of Electro Chemical Noise

From the Method menu, choose Electrochemical noise and then Transient.

1. Load the datafile ‘demoecn1’ from the \autolab\testdata folder.
2. From the Analysis menu choose Spectral noise analysis.
3. Choose a Hanning Window, check subtract offset, and the Result type: E(f) and I(f).
4. By clicking OK, a spectral analysis is performed on the Potential and the Current components of the noise signal.

Fig.13 *Example Electrochemical Noise analysis*



2.9 iR-compensation

When your Autolab is equipped with a PGSTAT12/20/30/100, you are able to measure the uncompensated resistance in your electrochemical cell and to compensate for this resistance. The GPES software provides two methods to do this: iR Interrupt and Positive feedback (see Chapter 3 for more details). This example is meant to make you more familiar with both options. Before starting, please connect the WE connector of the cell cable to WE(c) on the dummy cell.

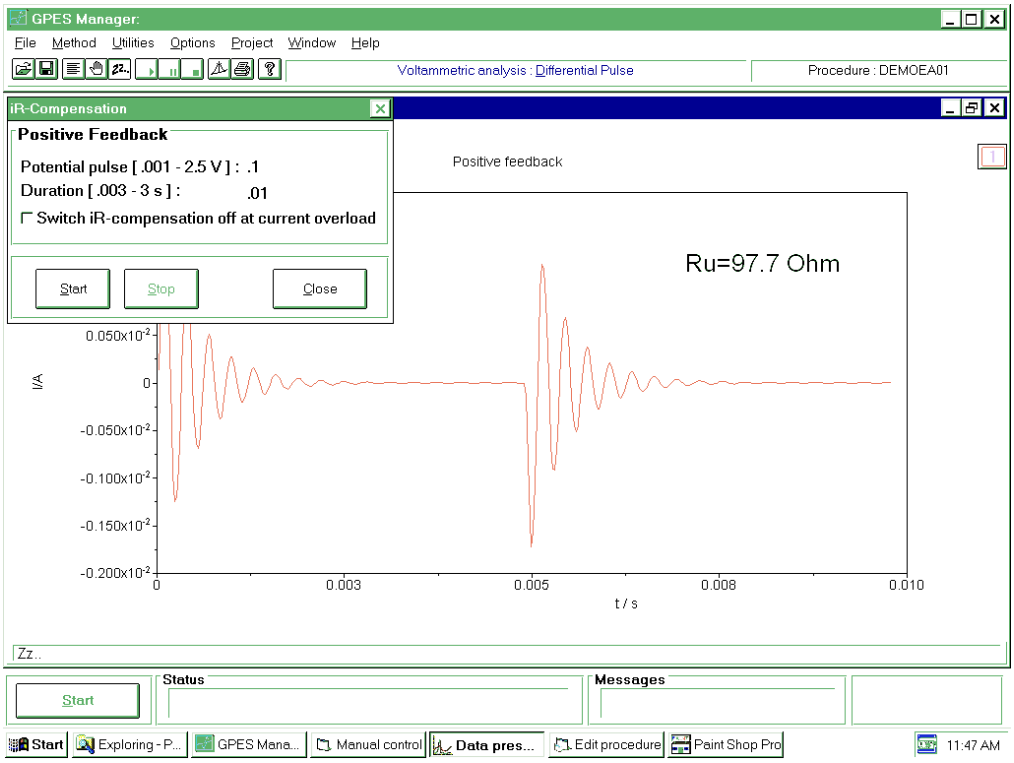
I-interrupt

a. Under the Utilities option in the GPES window, please choose I-interrupt, the iR-compensation window will appear. In the manual control window please type 1.0 V in the potential panel, and check the 1 mA Current range checkbox. You can now switch the cell on, by clicking the button in manual control.

b. In the iR-compensation window, please give the following values: Range =10V; Duration of interrupt =0.001 s; First marker =15; Second marker =35. The current will now be interrupted for 0.001 s, and the decay of the potential in time is measured. Please click the Measure button. After a short time, in the result panel a value of about 100 should appear. When you want to compensate for 90% of this value (never use 100% of the measured value!), you can do this by typing the value in the iR-compensation panel in the Manual Control window. After clicking the iR-compensation button the program will automatically compensate the measurements for the value given.

Positive feedback
With positive feedback you can give in values for the resistance yourself, and you can see when the current starts to oscillate, i.e. when you have overcompensated the resistance.
a. Please choose the Positive feedback option in the Utilities menu, an iR-compensation will appear in which you can type the following values:
Potential pulse = 0.1 V; Duration = 0.01 s. Connect dummy cell (C) and put the current range to 1 mA. After pressing 'start' the program will start applying potential pulses. By giving different values in the iR-compensation panel and watching the change in the i-t curve you can check how high the uncompensated resistance is. Please check the change after typing a value of "95". Now do the same after typing "130", you will see oscillations appearing, you have now done overcompensation. Please note that if you reach a value where the current starts to oscillate, you should use 90% of this value during your measurements.

Fig. 14 *Effect of overcompensation of the iR-drop*



2.10 Detection of noise problems

In the GPES software an option is available to detect noise problems. Since noise is encountered frequently in electrochemical research, it is useful to become familiar with the detection of problems caused by noise. In GPES, the Check Cell option under the Utilities menu, provides the option to detect noise.

Please connect the red banana plug to the WE(c) connection on the dummy cell. In order to generate some noise, please connect an unshielded cable between the blue banana plug and the RE connector on the dummy cell, and place part of this unshielded cable over the monitor of your computer. In manual control please check the 100 nA Current range checkbox.
After selecting the Check Cell option, the Check Cell window appears. After pressing the measure button, the program will start checking the electrode connections, and will then measure the noise level. With the unshielded cable over the monitor, you will see the current levels in red and the software will give you a warning that the noise level is too high. Please redo the measurement without the unshielded cable. You will now see the current levels in black indicating that the noise level is acceptable.
Please use this option if you have doubts about the noise level in your system.

3. The GPES windows

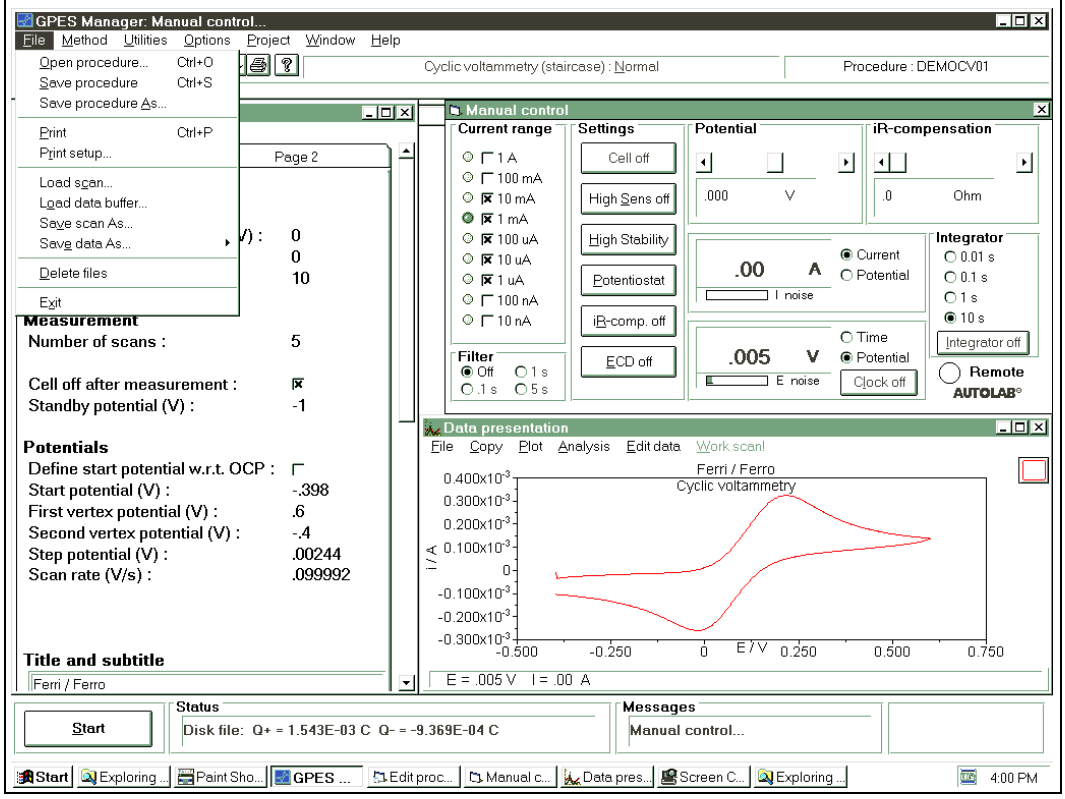
3.1 GPES Manager window

The title bar of the GPES Manager window contains several options i.e. File, Method, Utilities, Project, Window, Help.

File menu

This menu contains options which are usually present in Windows programs.

Fig. 15 *The File menu*



Open procedure

A procedure is a file containing all the experimental parameters. It contains measurement parameters, potentiostat/galvanostat settings, and graphics display values. The extension of the file which is mentioned in the "File name" field should not be changed.
The directory in which the procedure file is stored is called the procedure directory. When the directory in the Open procedure window is changed and a procedure file is

successfully loaded from this new directory, this new directory becomes the new default procedure directory.
Normally only files with the current method are shown in the load window. By selecting Show all GPES files in File dialog box (Utility menu), all procedures are displayed and can be selected.
It is also possible to load procedure files from the DOS version GPES 3. If this is required, click the "List Files of Type" drop down button and select the proper option.
It is also possible to load a procedure from other methods/techniques than the current one. The program will change automatically to the method described in the selected procedure. See the Dropdown menu called "List Files of Type".

Save procedure

This option will save a procedure under its current name in the procedure directory.

Save procedure as

Allows to store a procedure on disk in the procedure directory with a different name as the current one. Please use the default file extension as mentioned in "File name" field or omit the extension. In the latter case the correct extension will be added.

Print

The Print menu window appears after selecting this option. The Print select panel allows to choose between the print-out of the measured data, a dump of a window, and the print of a template consisting of a user-defined set of measurement parameters and a copy that can be scaled of the current graph.
The Setup template option allows to edit the template. The parameters on the template can be selected using the Insert menu option.
The parameter position can be dragged over the screen with the mouse. The comment text as well as the attribute of the item with focus can be edited by double clicking on it. If you have changed the template according to your requirements, please do not forget to save it (see corresponding File option).
The rectangle in the template is the Graph frame. The focus is on the frame after a click in the frame. If the left hand mouse button is pressed down within this frame it can be dragged.
If the right hand button is clicked, the lower right corner of the frame jumps to the mouse cursor and is subsequently attached to the mouse cursor. This allows you to adjust the frame size. After a click with the left hand mouse button the attachment is broken. The appearance of the graph in the print out of the template depends on the actual size and shape of the Data presentation window.
The print of the template will cover half a page if printed in ‘portrait’ and a full page if printed in ‘landscape’. See print setup. On the print-out the parameter values also appear. The print-out can also be previewed (see corresponding File option).

Load data (sometimes called Load scan)

Allows to load previously measured data from disk.
It is also possible to load data files from the DOS version GPES3 or data files of other methods or techniques than the current one. If this is required, click the "List Files of Type" drop down button and select the proper option. You can select multiple files at a time by using <Shift> or <Control>, combined with the mouse action. This allows

you to load the work data as well as 10 overlay files. After this action it is possible to exchange the work data by clicking ‘Work scan’ on the Data presentation window.

Save data

Store the most recent measured data under the current procedure name on disk. In case of cyclic and linear sweep voltammetry the user is asked to select a scan number first. The data are stored in the so-called data directory, together with the corresponding procedure parameters.
When more than one scan is recorded in Cyclic voltammetry, it is possible to save the previously measured scan while the measurement is going on. This option is available at the File menu on the Data presentation window. The option is called ‘Quick save of previous scan’. This option can also be activated by typing ‘SAVE’ on the keyboard. The path and the name of the file can be specified on page two of the Edit procedure window (‘Direct output filename’). The last five characters of the file name will be used as the scan number.
Please note: These files can be overwritten during another measurement session with the same procedure.

Save scan as

This options allows to save a scan in Cyclic and Linear sweep voltammetry.
First, if more than one scan is recorded, a menu is shown from which the user can select the number of the scan to be saved.

Save data as

Similar as the previous option but the name of the file name containing the data can be specified. For cyclic and linear sweep voltammetry a submenu is presented from which the required data format can be selected.

Save data buffer as

This option can only be selected for cyclic and linear sweep voltammetry. The whole data memory is dumped on disk in binary format in the data directory under a user specified procedure name, together with the corresponding procedure parameters. This is the only save option which stores all relevant data. If a buffer is reloaded, all data treatment and save option are open for use.

Export to scanno. vs Q+,Q- file

When a cyclic voltammogram is observed with more than one scan it is possible to save the observed cathodic and anodic charge data against the scan number. The file, with the extension .Q&Q, has the following layout:

ScanNr	Q+ (C)	Q-(C)
1	1.697E-07	-2.351E-07
2	1.670E-07	-2.365E-07
3	1.671E-07	-2.363E-07
4	1.672E-07	-2.357E-07
5	1.674E-07	-2.356E-07
6	1.675E-07	-2.361E-07
7	1.669E-07	-2.356E-07
8	1.667E-07	-2.358E-07
9	1.674E-07	-2.364E-07
10	1.675E-07	-2.355E-07
.		
.		

Export Chrono data

This option is only available for cyclic voltammetry. It allows to store the chrono-amperometric data which are recorded at the vertex potential. See the input parameters under the heading "Chrono-amperometry" in the Edit procedure window

Export to BAS-DigiSim data

This option is only available for cyclic voltammetry. Save the current active in such a format that it can be read by the program DigiSim. This is an ASCII-file with the default extension .TXT.

Export data buffer to text file

This option can only be selected for cyclic and linear sweep voltammetry. As in the previous option the whole data memory is stored on disk, but in this case in a readable ASCII-format. The file consists of several columns. The first column is the potential (or current in galvanostat mode) and the other columns are the measured currents for subsequent scans (potentials in galvanostat mode). The first row indicates the scan number. The separator c.q. delimiter between two columns is a TAB character. The default extension of the file is .TXT. They are meant to be read by MS-Excel, they cannot be read by GPES. In order to create a nice and properly columned file, each scan should have the same number of points. This means that the Reverse button should not have been clicked. Also an interruption of a scan by pressing ESC should be avoided.

The layout of the text file saved with the ‘Export data buffer to text file’ also contains some important procedure parameters:

```
Date: 26-May-97
Time: 14:12:17

Exp. Conditions:
Linear sweep voltammetry
Begin potential (V) = .0000
End potential (V) = 1.0000
Step potential (V) = .02441
Scan rate (V/s) = .99992
Equilibration time (s) = 10
Number of Data Points =  42

 Potential              Scan 1              Scan 2
 0.024414           -1.191406E-07       -1.232910E-07
 .
 .
```

Load data buffer

This option can only be selected for data from cyclic and linear sweep voltammetry. Allows to load the complete set of scans (see Save data buffer). This is only possible if in the start-up menu "Autolab applications" has been chosen.

Delete files

This option allows to delete procedures and measured data files. The File window shows only the procedure files. A selected procedure will be deleted from disk together with corresponding data files. A delete action can not be undone.

Exit

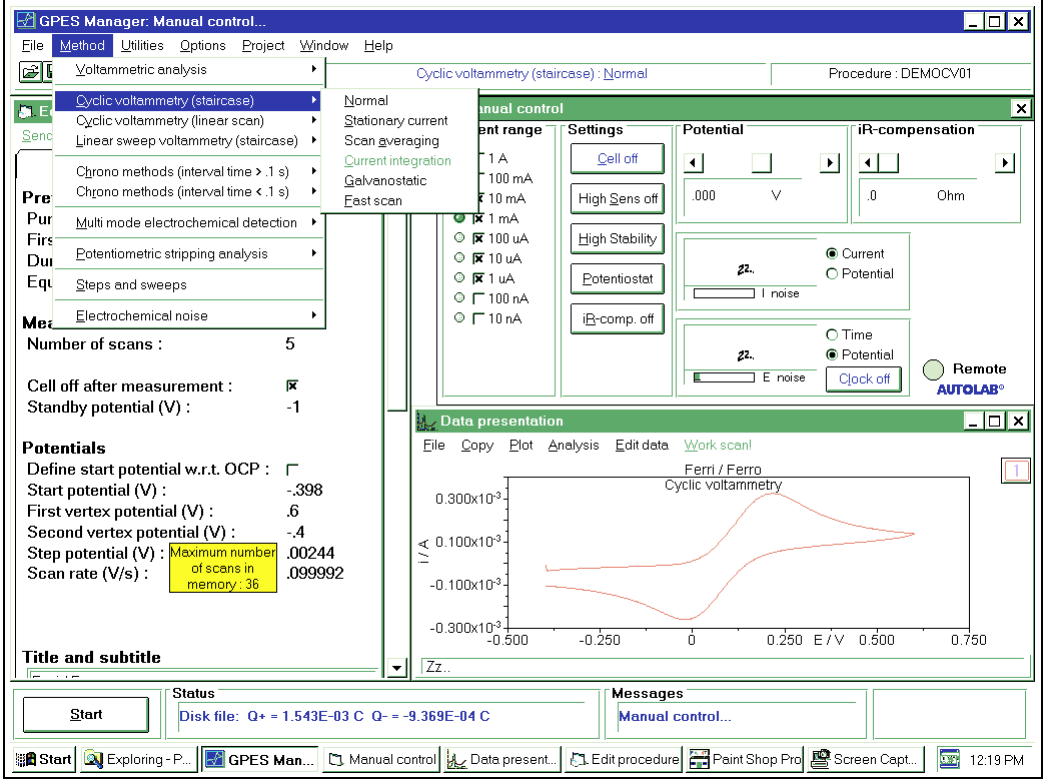
The GPES window will be closed and the program is exited. The program settings are stored on disk.

Method

The required electrochemical technique can be selected with the Method menu The type of experiment parameters in the Edit procedure window will change depending on the selected technique.

For more information see the manual section on “Electrochemical methods”.

Fig. 16 *The Method menu*

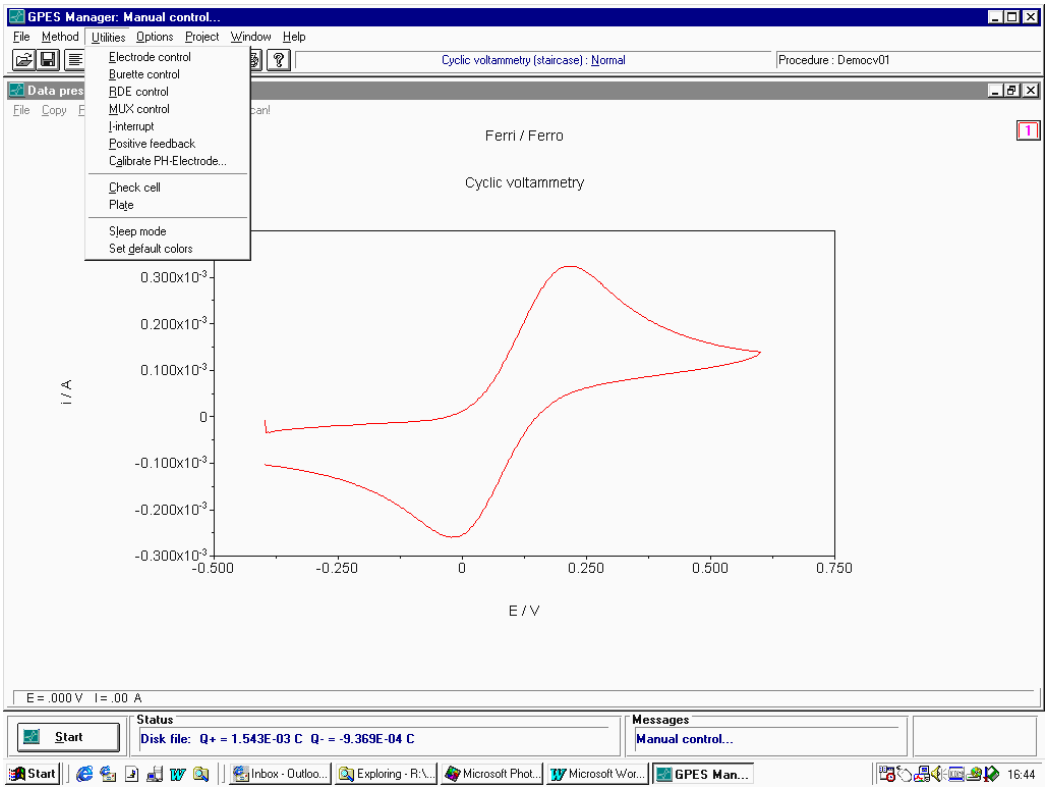


The settings in the File menu and the data analysis also depend on the type of technique. More details about the available methods can be found in a separate chapter.

Utilities

The Utilities window allows to select electrode control, burette control, I-interrupt, positive feedback, hardware, check cell, plate, sleep mode, set colour defaults, and options.

Fig. 17 *The Utilities menu*

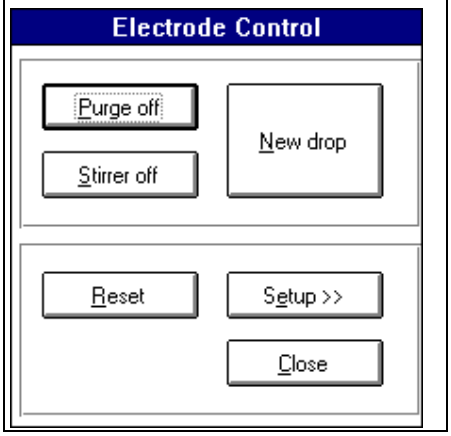


Electrode control

The Electrode control option allows to operate a static mercury drop electrode which is connected via an IME-interface to the Autolab. The stirrer can be switched on and off, the purge valve can be opened and closed, and a mercury drop can be created.

The Reset button will reset the digital I/O port of the Autolab instrument. The Purge and Stirrer will be switched off. This option is not accessible when no static mercury drop electrode is connected to the Autolab.

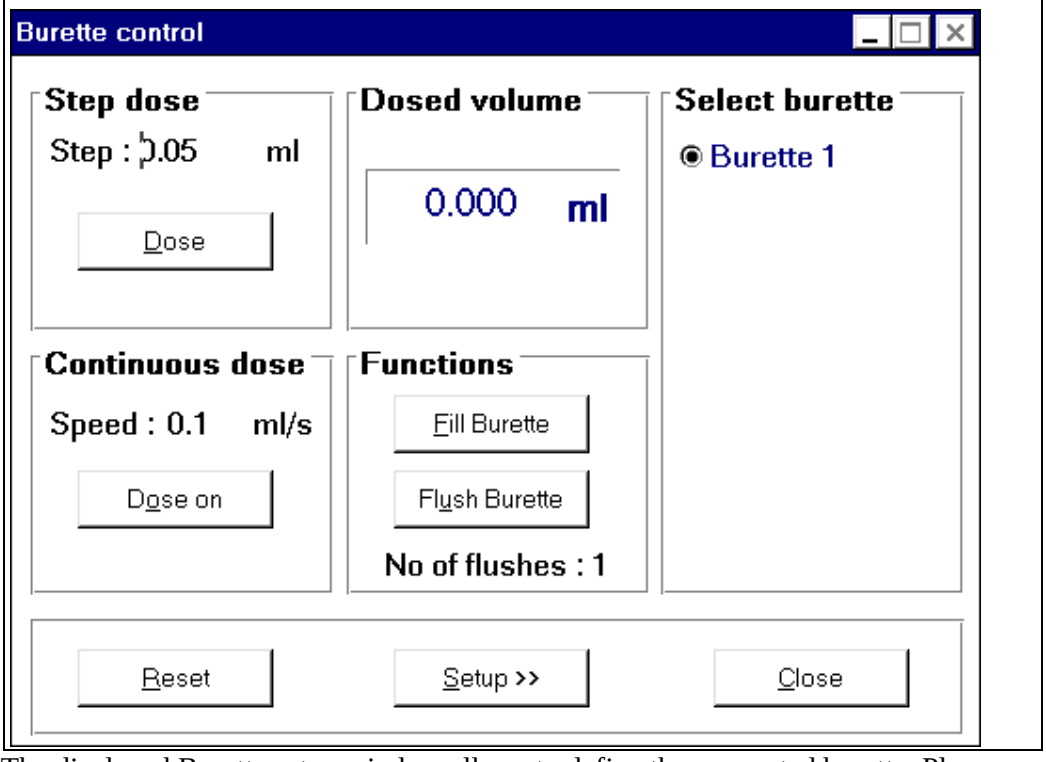
Fig. 18 *The Electrode control window*



Burette control

The burette control option allows to control motorburettes connected to Autolab via the DIO48 module. Consult the "Installation and Diagnostics" guide about the type of burettes that can be connected. First click the Setup button. Then select the burette.

Fig. 19 *The Burette control window*



The displayed Burette setup window allows to define the connected burette. Please consult the manual of your burette for the parameters.

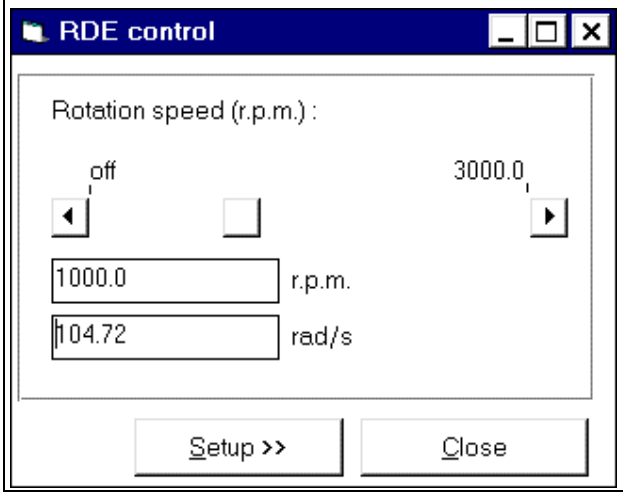
The ‘Maximum time to check for Ready’ is the maximum wait time for the software to receive a "ready" signal from the burette.
The DIO port used is shown on your Autolab front.
The Dose button will dose the amount specified above. The dosed volume is displayed.

The Dose on button will dose with the speed displayed above.
The Reset button will give a ‘reset’-command to the burette and sets the dosed volume to zero.

RDE-control

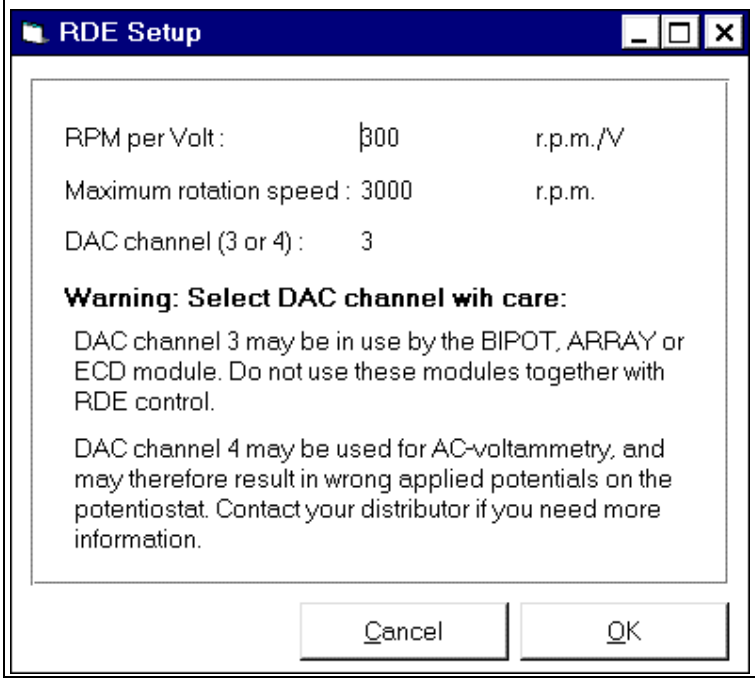
In order to control an external Rotating Disk Electrode (RDE), an option is available in the Utilities menu of the GPES manager. In Hardware configuration, an external RDE should be specified. After selecting the RDE control item the following window appears:

Fig. 20 *The RDE control window*



With the scroll bar it is possible to control the rotation speed of the RDE. You can also enter the number of rotations per minute by changing the r.p.m. edit field or enter the rotation speed in radials per second in the rad/s edit field.
After pressing the Setup button the RDE setup window appears:

Fig. 21 *The RDE setup window*


RDE Setup
RPM per Volt : 300 r.p.m./V
Maximum rotation speed : 3000 r.p.m.
DAC channel (3 or 4) : 3
Warning: Select DAC channel wih care:
DAC channel 3 may be in use by the BIPOT, ARRAY or ECD module. Do not use these modules together with RDE control.
DAC channel 4 may be used for AC-voltammetry, and may therefore result in wrong applied potentials on the potentiostat. Contact your distributor if you need more information.
Cancel
OK

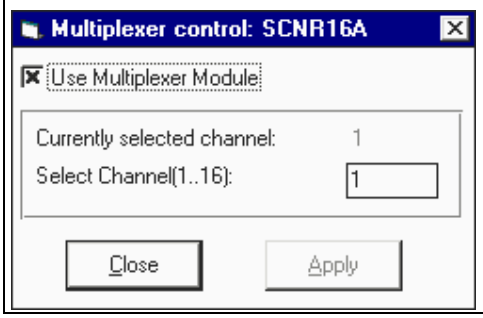
In this screen you can configure the RDE.

MUX control

The channel number of the SCNR16A, SCNR8A or MULTI4 module can be selected manually by the operator before starting the measurement procedure:

1. Open the MUX control dialog by selecting MUX control from the Utility menu. The dialog screen shown in the figure below will pop up.
2. Enable the checkbox “Use Multiplexer Module”.
3. Choose the desired channel.
4. Pressing <Apply> or closing the dialog screen will set the selected channel.
5. The active channel number will be indicated in the Manual control window.

Fig. 21a *The MUX control window*



If you want to return to direct connections, you can disable the “Use Multiplexer Module” checkbox.

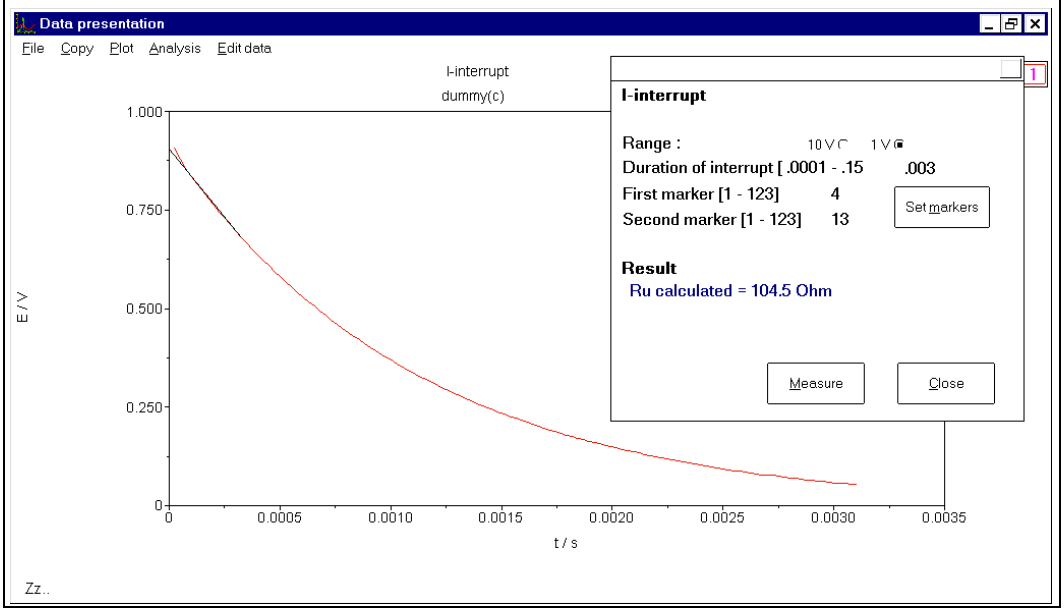
I-interrupt

The I-interrupt option provides a method to determine the Ohmic resistance of the cell. This option is only available when the Autolab is equipped with a PGSTAT12/20/30/100 potentiostat/galvanostat. The technique involves switching off the current and measuring the potential-time curve. As soon as the current is switched off, the potential difference across the Ohmic resistance is zero and the charged double layer is discharged. By extrapolating the curve following a straight line to the beginning (time is zero), the iR-drop is calculated. Since the current is measured just before switching off the cell, the uncompensated resistance is calculated.
It will be clear that for a proper calculation of the uncompensated Ohmic resistance Ru, the current must be known very precisely. Proper measurement must be done at a potential where the current is high enough to be measured and the applied current range must be adequate to measure the current. For proper measurements, the current must be at least in the order of 1 mA.
Also make sure that the current at the applied potential, before the current interruption, can be measured sufficiently accurate. Therefore select a proper current range, which means that the current should be in the order of the selected current range.
It is recommended to switch off the iR-compensation, see Manual control window.
In order to get an accurate value for the uncompensated Ohmic-drop, the I-interrupt measurements should be done at the highest possible speed. If an ADC750 module is present in the Autolab system it is possible to use this module, in order to speed up the measurements to 750 kHz.
Before measuring you need to specify the potential range at which the I-interrupt is performed. If the potential is within the limit of -1V to 1V, specify 1 V range. If the potential is outside this range, specify 10 V range.

On the iR-compensation window that appears, several parameters need to be specified.
Duration of the interrupt: The interruption period; a reasonable value is .001 to .01. The shorter the better.
First/second marker: The data point numbers between which a straight line is fitted. In total 20 points are measured.

After the parameters have been specified, the Measure button can be clicked. The measured data are subsequently plotted and the straight line is drawn. The calculated uncompensated resistance is printed in the Result panel.
Now the Set marker button is available. When clicked you can change the First and Second marker value by clicking two data points on the measured curve.

Fig. 22 *Example of the results of a current-interrupt measurement*



The calculated uncompensated resistance can be used as an estimated start value to be used in the Positive feedback option. See next section.

WARNING: *Too high Ohmic drop compensation can cause oscillation of the potentiostat, which may cause damage to the working electrode.*

An example of the use of I-interrupt is given in the chapter 'Getting started with GPES'.

Positive feedback

The Positive feedback option provides an interactive method for determination and compensation of the Ohmic resistance of the cell. This option is available only when the Autolab is equipped with a PGSTAT12/20/30 or 100 potentiostat/galvanostat. The technique of measurements is based on measuring the current response after applying a potential pulse. The current response is displayed on the screen. The current response depends on the actual values of the Ohmic resistance and the doublelayer capacitance. Compensation of the Ohmic resistance results in a faster decaying of the charging current. When the compensation is near 100%, the measured current response will show damped oscillation.

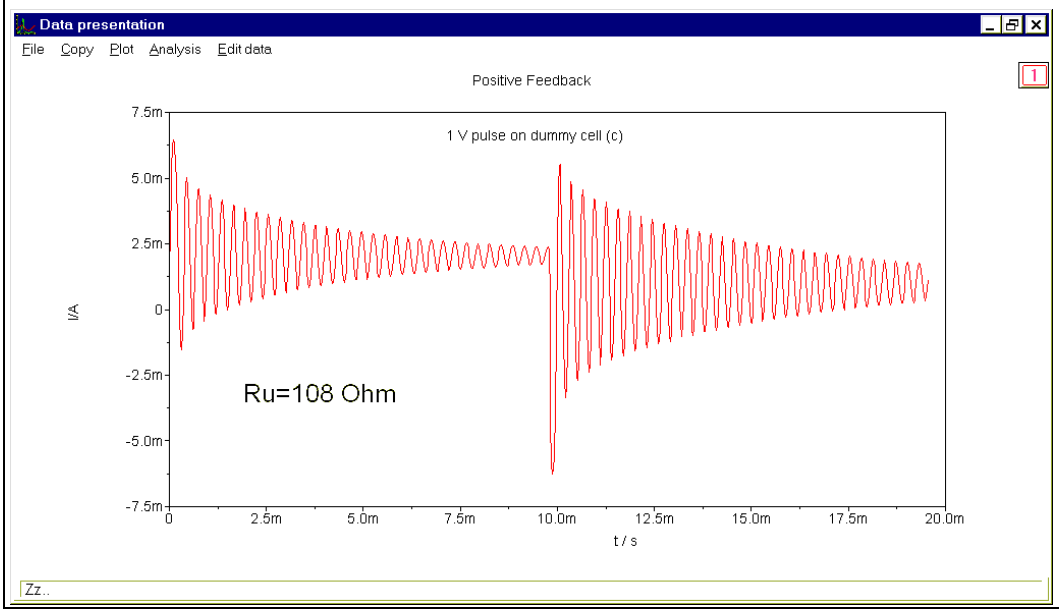
Three parameters need to be specified.
Potential range: Can be either 10 Volt or 1 Volt. If the expected measured potential is < 1 Volt or > -1 V, select the 1 Volt range. Otherwise select 10 V range.
Potential pulse: The height of the applied potential pulse. A reasonable value is 0.1V.
Duration: The period during which the current versus time data are measured. This is twice the duration of the pulse. A reasonable value is 0.01 s.

When the Start button is clicked, current versus time measurements are done repeatedly and the iR-compensation of the potentiostat is switched on. Now the compensated resistance can be varied with the iR-compensation slider on the Manual control window.

When "Switch iR-compensation off at current overload" is checked, the cell will be switched off when the current exceeds about 8 times the current range value. This normally occurs when the potentiostat oscillates because the compensated resistance is too high.

WARNING: *Too high Ohmic drop compensation can cause oscillation of the potentiostat, which may cause damage of the working electrode.*

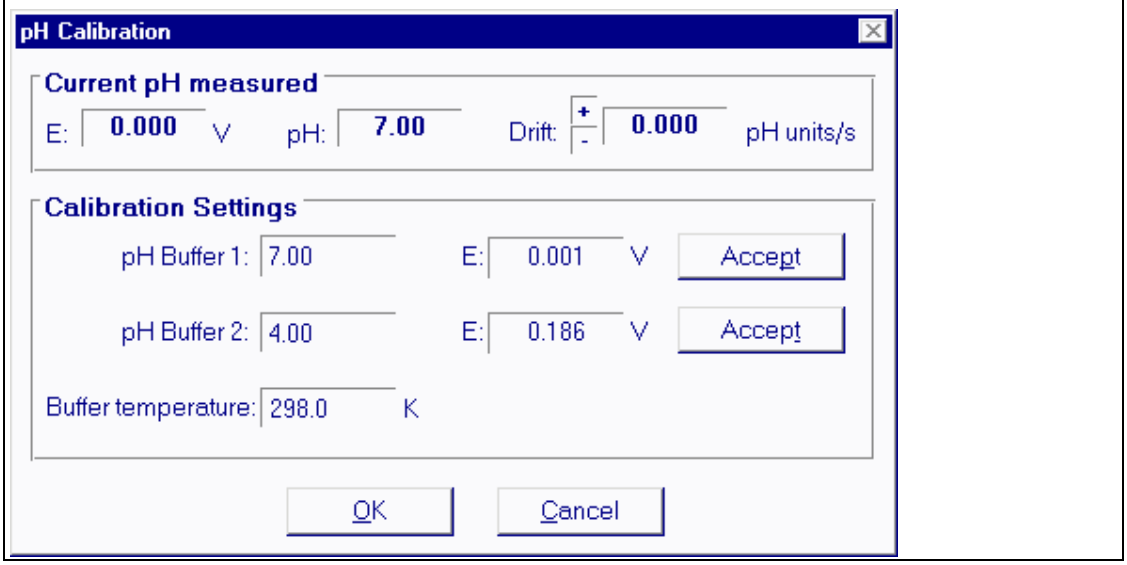
fig 22a. *Effect of overcompensation of the iR-drop*



Calibrate pH-Electrode

This window allows to calibrate pH electrodes. It is possible to specify two buffer solutions and the calibration temperature. Measuring the pH as a 2nd Signal gives the possibility to specify a measurement temperature. The pH is corrected for temperature.

Fig. 22b *The Calibrate pH-Electrode window*

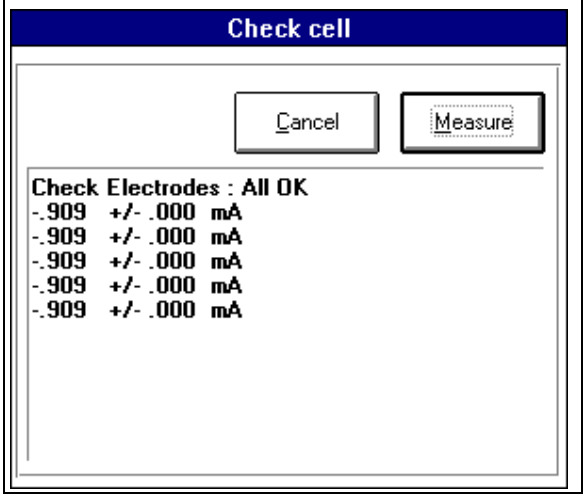


When the value for a pH buffer is Ok press the Accept button. The OK button will actuate the calibration for the measurement.

Check cell

The Check cell option allows to check the electrode connections and the noise level. When selecting this option an empty window appears with a Cancel and a Measure button. First apply a proper electrode potential and current range on the Manual control menu. Subsequently click the Measure button. The window will subsequently give information about the Electrode connections by comparing the applied and measured electrode potential.
Also during 0.100 second the current is sampled at the highest rate possible.

Fig. 23 *The Check cell window*



The next figure shows a noisy signal displayed after pressing Measure. The plot clearly shows periodic noise with a frequency of 50 Hz. After optimising the cell simply by removing the unshielded cable of the reference electrode, the same measurement shows a better signal-to-noise ratio.

Fig. 24a *A noisy signal*

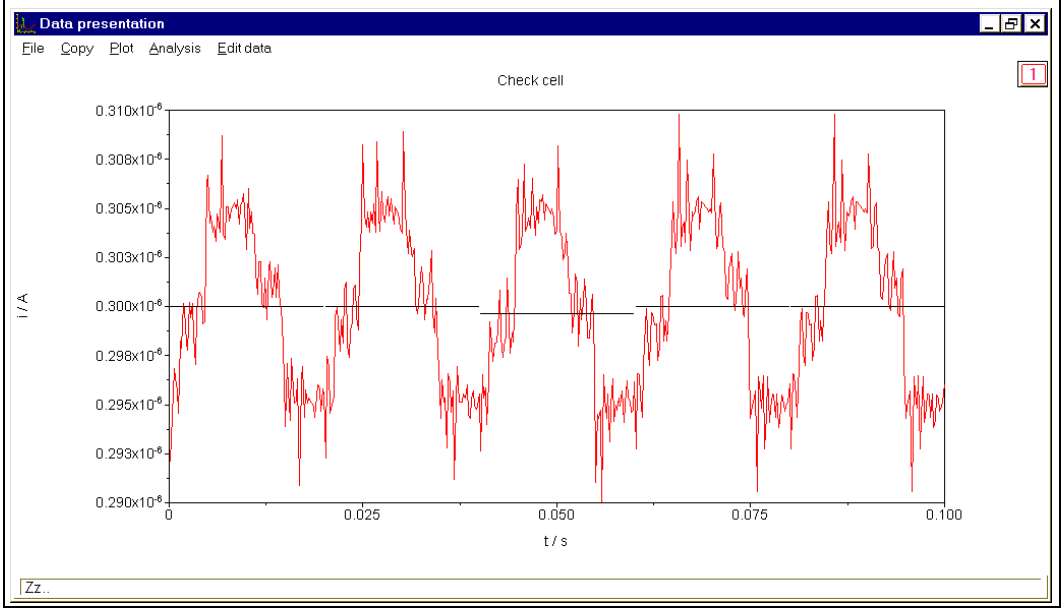
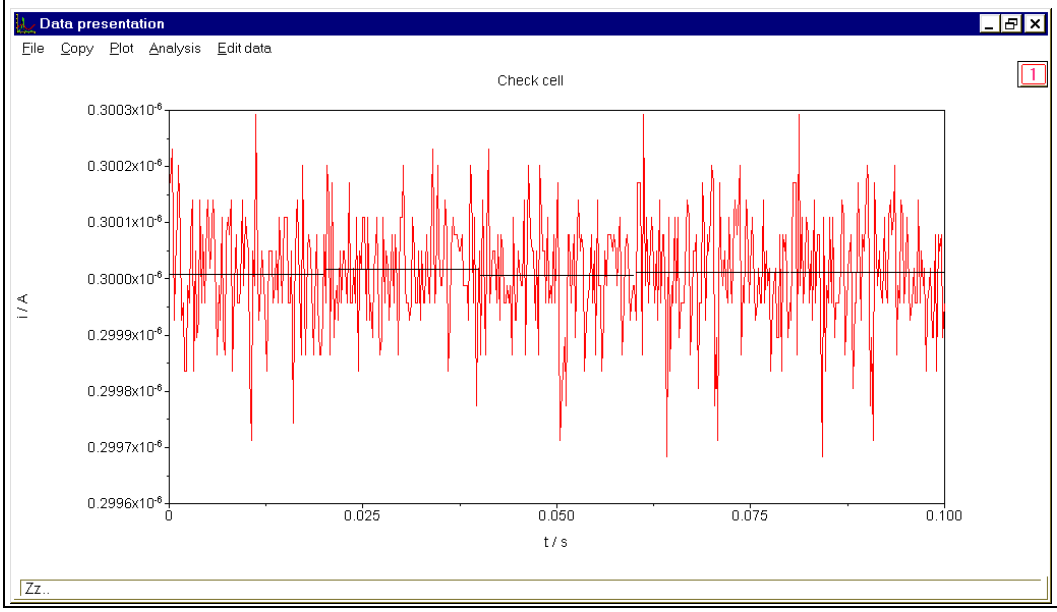


Fig 24b *A better signal-to-noise ratio*

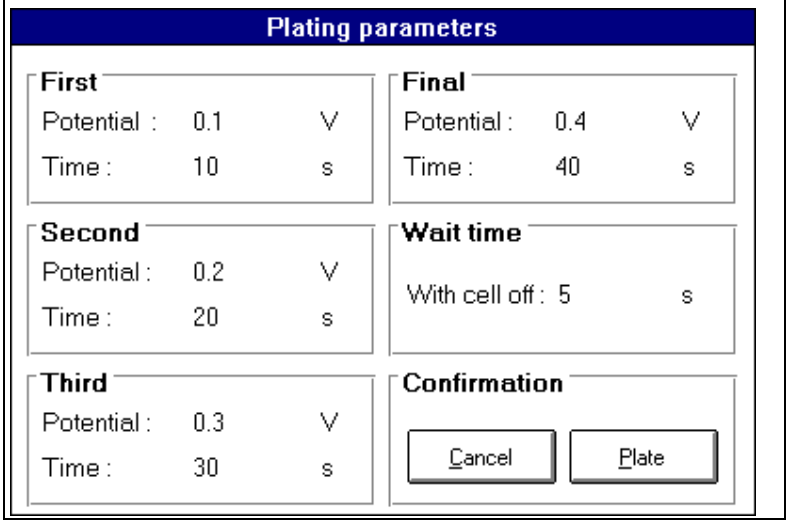


The measured current and the five average values over one power cycle, normally 0.020 second, are plotted in the Measure window. The obtained five average values and their standard deviations are given in the Check cell window. A judgement about the noise level and the selected current range are given. See also Chapter 16 of the "Installation and Diagnostics" guide. It is possible, after an improvement of e.g. the cell configuration, to re-Measure. By pressing Cancel the Check cell window disappears.

Plate

The Plate option will display a window in which three plating potentials, a 'cell off' wait time and a final potential can be specified.

Fig. 25 *The Plate window*



The three plating potentials are alternated with the 'cell off' time. Subsequently the 'final' potential is applied.

Sleep mode

When the Sleep mode option is clicked, newly measured data will no longer be displayed in the Manual control window and the Data presentation window. This option is useful when during slow but time consuming measurements a spreadsheet program or word processor is activated. The Sleep mode will minimise the time required by GPES. During the sleep mode, the measuring part of GPES will stay active. In this way data are measured but not displayed.

Project

The Project option allows to execute a large number of electrochemical experiments unattended. A project encompasses a number of tasks which have to be executed sequentially. Sometimes this is called batch mode processing. A measurement procedure is normally activated by clicking the Start button in the lower left corner. It is also possible to start a procedure by creating and subsequently executing a project. A project can be created by selecting the Project edit option. First you have to indicate whether a new project should be made (New option) or an existing project file should be opened (Open option). An example of a project is delivered with the GPES4 program in the testdata directory.
After editing a Project it can be stored on disk under its current name (Save option) or under a new name (Save as option).
When Edit is selected the Edit project window appears with two options on the main menu bar. The Check option checks whether there are syntax errors in the project commands. The Edit option provides the standard Cut, Copy and Paste option.

Below you will find the Project script language definitions and rules.

Project command rules

- Both upper and lower case characters can be used in command lines.
- Space characters are ignored.
- If during the execution an error occurs the project continues with the next line.
- An error message will be printed in the Results window.
- One line per command.

- The following commands are allowed:

; <string>		
rem <string>	:	comment
Procedure!Method = <method id>	:	define the electrochemical method
Procedure!Open("<filename>")	:	open a procedure file
Procedure!SaveAs("<filename>")	:	save the procedure file
Procedure!Start	:	start the execution of the procedure
Procedure!AddToStandby(<real>)	:	Add a value to the standby potential. Only available for Chrono-Ampero- and Chrono-Coulometry experiments.
Procedure!AddToPotlevel(<real>)	:	Add a value to all specified potential levels. Only available for Chrono-Ampero- and Chrono-Coulometry experiments.
Procedure!AddToPotlevelEx (<n>,<real>)	:	Add a value to a specific potential level (n). Only available for Chrono-Ampero- and Chrono-Coulometry experiments.

Procedure!AddToCurlevelEx (<n>,<real>)	:	Add a value to a specific current level (n). Only available for Chrono-Potentiometry experiments.
Dataset!Open("<filename>")	:	open a previously measured data file
Dataset!SaveAs("<filename>")	:	save the measured data
Dataset!AutoNum = <n>	:	enable auto-numbered files names, starting with number <n>
Dataset!AutoReplace ("<string>")	:	specify the string which should be replaced by a number in the <filename> for auto-numbered files.

Example (see below)

```
;Start file numbering with number 5
DataSet!AutoNum = 5
;Replace string xxx
DataSet!AutoReplace("xxx")
;Save Automatic number file
DataSet!SaveAs("c:\autolab\data\filexxx")
;The first file is now saved as
c:\autolab\data\file005.ocw
```

Please note:
When a FRA-project is started from GPES and the FRA-project and both projects contain the command 'DataSet!AutoNum = <n>', then the number of the FRA-project is overruled by the number in the GPES-project.

Dataset!PeakSearch	:	perform automatic peaksearch with baseline correction
Dataset!Selectscan = <scanno>	:	select a recorded scan number in cyclic or linear sweep voltammetry for further processing
Dataset!MinMax	:	find the minimum and maximum value in a dataset
Dataset!Smooth = <smooth level>	:	smooth the data using the Savitsky and Golay algorithm. The smooth level can be an integer number between 0 and 4. Note that after the execution of the project the smoothed data are replaced by the originally measure data
Dataset!SaveQ&Q(“<filename>“)	:	store the anodic and cathodic charge versus scan number (Q&Q files) for cyclic voltammetry data. The filename must be specified without an extension.

Dataset!SaveImpedance (“<filename>“)	:	project command to store impedance data measured for AC-voltammetry. The extension is .IMP. The filename must be specified without an extension.
Dataset!Subtract("<filename1>", <filename2>","<filename3>")	:	subtract files and save the result in another file. <filename3> = <filename1> - <filename2>
Utility!SetRDERPM = <rpm>	:	set the Rotating Disk Electrode to a specific rotation speed. The set-up of the RDE is made in the RDE control option under Utilities.
Results!Clear	:	clear the Results window
Results!SaveAs	:	save the Results window
System!Run("<filename>")	:	execute another program and wait until it terminates. The System!Run command search for the program file with the next sequence: .PIF .EXE .COM .BAT
System!Beep	:	give a beep
Print!Template	:	print a hardcopy according to the template
Print!Plot	:	print a hardcopy of the Plot window
Print!Procedure	:	print a hardcopy of the measurement procedure
Print!Results	:	print a hardcopy of the Results window
FRA!Start("<filename>")	:	start a FRA project file from GPES "<filename>" should be a FRA project file
Utility!Channel = <n>	:	sets the active channel to <n>. The MUX will be automatically enabled when necessary.
Utility!NextChannel	:	increase the active channel number with one. If the channel is not available, the active channel number is set to 1.

Please note:
The last 2 commands are available in the GPES and FRA programs. However, for FRA projects that are called from within GPES projects, all channel switching commands in the FRA project scripts are ignored. In such cases, the GPES project will have exclusive control over the channel selection.

Utility!Delay = <n>	:	hold the project for <n> seconds.
Repeat(<n>) EndRepeat	:	with the Repeat and EndRepeat commands it is possible to repeat a part of the project <n> times. You can nest these commands maximal 5 times.
ForAllChannels("<filename>")	:	executes the active measurement procedure for all available MUX-channels and store the results in the <filename> adding 3 characters to the filename as channel number counter, for example: fname001, fname002, etc. .
DIO!SetMode("<Connector>", "<Port>","<Mode>")	:	set the mode of a port of the DIO.
DIO!SetBit("<Connector>","<Port>", "<n>","<Bit>")	:	set a single pin of the DIO on or off.
DIO!SetByte("<Connector>","<Port>" ,"<n>")	:	set a port of the DIO to the specified value.
DIO!WaitBit("<Connector>","<Port>", "<n>","<Bit>")	:	wait until a single pin of the DIO is set on or off.
DIO!WaitByte("<Connector>","<Port>", "<n>")	:	wait until a port of the DIO is set to the specified value.
Burette!DoseVolume (<Burette number> ,<Dose volume>)	:	dose a specified volume to the specified burette.
Burette!Fill (<Burette number>)	:	Fill the burette.
Burette!Flush (<Burette number> ,<Number of flushes>)	:	flush the burette.
Burette!Reset (<Burette number>)	:	Will give a 'reset'-command to the burette.

- The <method id> can be:

VA	:	voltammetric analysis
CV	:	cyclic or linear sweep voltammetry
CM	:	one of the chronomethods
ECD	:	multi mode electrochemical detection
ECN	:	electrochemical noise
SAS	:	steps and sweeps
PSA	:	potentiometric stripping analysis
<string>	:	line of text
<filename>	:	a filename without extension, but including a directory name
<scanno>	:	the number of a recorded scan
<rpm>	:	rotations per minute

The FRA project file can only be executed if the FRA-program is already running. For more information about the combination of GPES and FRA, see Appendix III in the GPES manual.

A special case occurs when the measurement should start at the open circuit potential. Normally the user is asked to click the Continue button, but in automatic mode the program continues by itself after 1 second.

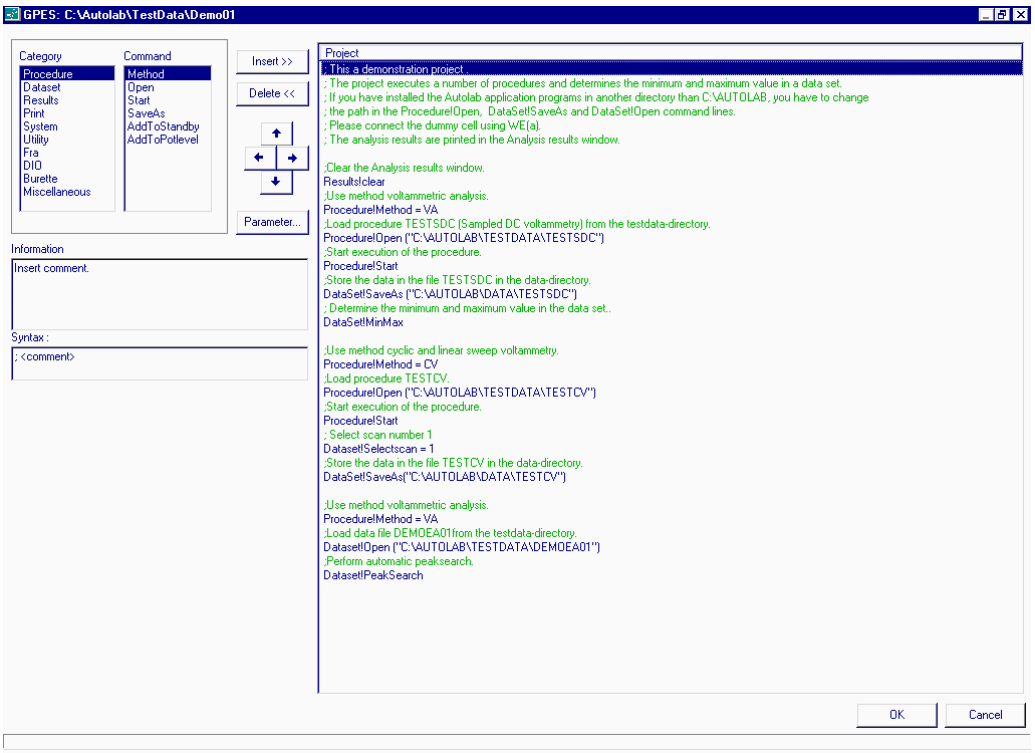
When no scan number is selected in cyclic or linear sweep voltammetry, the program uses the last recorded scan as default.

Examples of projects can be found in the files ‘Demo01.mac’ and ‘Demo02.mac’ present in the \AUTOLAB\TESTDATA folder.

Project wizard

The Project wizard provides an easy way of editing and/or defining a project. This option allows the user to pick project command lines from a list of all commands, insert them in a project and define the parameters. The window below gives a project Wizard overview.

Fig 26. *An example of a project inside the Project wizard*



Every project command can be inserted in the project, deleted or moved to another place. A short description of the command is given in the information and syntax box. Using the parameter button one can define the parameters that belong to that specific command.

Project examples

Example 1: Cyclic voltammetry on MUX channel 2 and 4

The following example of a GPES project will perform the "c:\autolab\testdata\testcv" procedure on channels 2 and 4, and stores the results in “c:\autolab\data\test channel 1” and in ”c:\autolab\data\test channel 4” :

```
Procedure!Method = CV
Procedure!Open("c:\autolab\testdata\testcv")
Utility!Channel = 2
Procedure!Start
Dataset!SaveAs("c:\autolab\data\test channel 1")
Utility!Channel = 4
Procedure!Start
Dataset!SaveAs("c:\autolab\data\test channel 4")
```

Example 2: Chrono amperometry on consecutive MUX channels

The following example will perform the "c:\autolab\testdata\testca" procedure on channels 1 to 4, and stores their results using automatic filename numbering. The result will be stored as “test scanner with cm 001”, “test scanner with cm 002”, “test scanner with cm 003” and “test scanner with cm 004” with the number corresponding to the channel:

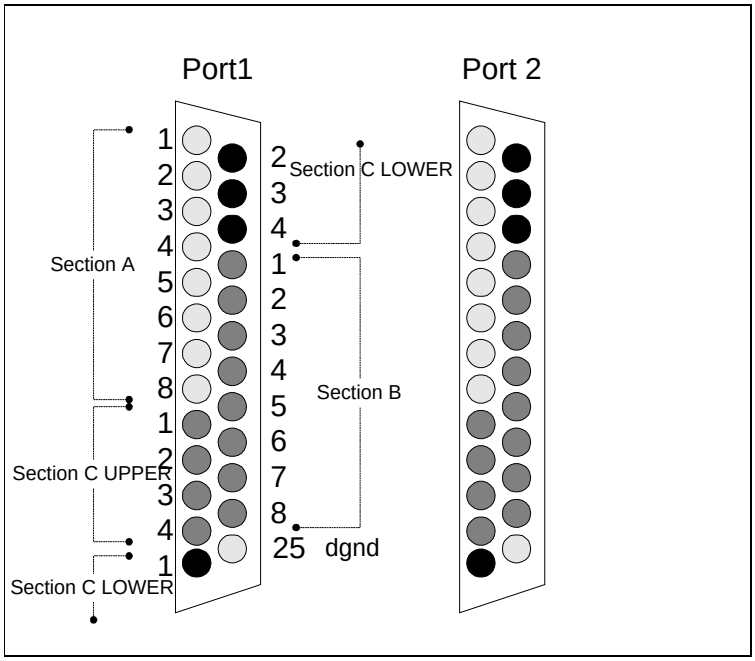
```
Procedure!Method = CM
Procedure!Open("c:\autolab\testdata\testca")
Dataset!Autonum = 1
Dataset!Autoreplace("xxx")
Utility!Channel = 1
Repeat(4)
    Procedure!Start
    Dataset!SaveAs("c:\autolab\data\ test scanner with cm xxx")
    Utility!NextChannel
Endrepeat
```

Example 3: Provide or receive trigger signals to or from DIO ports

These are the commands to set any of the pins on a DIO port of the Autolab instrument. They can for example be used to control a Metrohm 730 Sample Changer. Any of the pins can be set from low to high or the other way around, and can also be used to receive an input trigger. With the SetMode command, one specifies whether one wants to send or receive a trigger. SetBit allows to set one of the pins to on or off. SetByte can be used to set multiple pins to on or off.

```
DIO!SetMode("P1", "A", "OUT")
;On connector P1, port A, the mode is set to OUT, so ready to
send a trigger.
DIO!SetBit("P1", "A", "4", "ON")
;On connector P1, port A, Pin number 5 (pin number 1 has value 0)
is set ON (i.e. sends a trigger).
DIO!SetBit("P1", "A", "4", "OFF")
;On connector P1, port A, Pin number 5 is set OFF again.
DIO!SetMode("P1", "A", "IN")
;On  connector P1, port A, the mode is set to IN, so ready to
receive a trigger.
DIO!WaitBit("P1", "A", "2", "ON")
;The project will wait for an input trigger on P1, port A, Pin
number 3.
DIO!SetMode("P1", "A", "OUT")
;On connector P1, port A, the mode is set to OUT, so ready to
send a trigger.
DIO!SetByte("P1", "A", "3")
;On P1, port A, both pin 1 (2^0) and 2 (2^1) are set ON. In case
one wants to set Pin 3 and 5, one needs to set the value 40
(=2^3+2^5) instead of 3.
DIO!SetMode("P1", "A", "IN")
;On connector P1, port A, the mode is set to IN, so ready to
receive a trigger.
DIO!WaitByte("P1", "A", "3")
;On P1, port A,  the project is waiting for an input trigger on
both pin 1 and 2 .
;In case one wants to receive the trigger on Pin 4 and 6, one
needs to set the value 80 (=2^4+2^6) instead of 3.
```

Fig. 26a *Schematic overview of both DIO ports with PIN numbering for the different sections. Pin 25 is always the digital ground.*



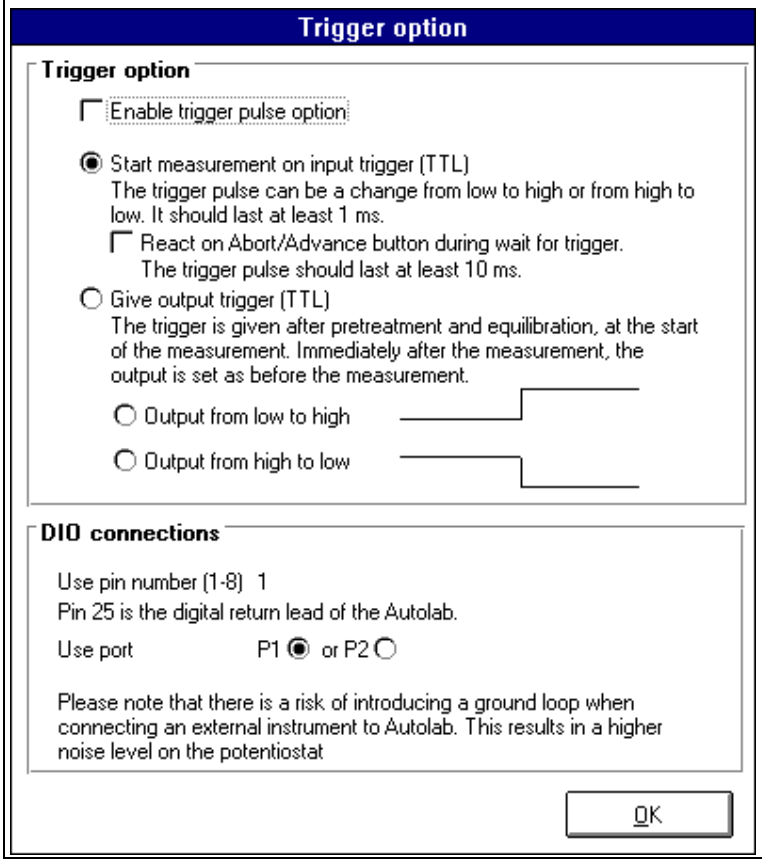
Options

The Options menu encompasses the following items.

Trigger

Under this item the option Trigger is present. After selecting this option the following window appears. In this window the trigger pulse can be configured.

Fig. 27 *The Trigger option window*


Trigger option
Trigger option
Enable trigger pulse option
Start measurement on input trigger (TTL)
The trigger pulse can be a change from low to high or from high to low. It should last at least 1 ms.
React on Abort/Advance button during wait for trigger.
The trigger pulse should last at least 10 ms.
Give output trigger (TTL)
The trigger is given after pretreatment and equilibration, at the start of the measurement. Immediately after the measurement, the output is set as before the measurement.
Output from low to high
Output from high to low
DIO connections
Use pin number (1-8) 1
Pin 25 is the digital return lead of the Autolab.
Use port P1 or P2
Please note that there is a risk of introducing a ground loop when connecting an external instrument to Autolab. This results in a higher noise level on the potentiostat
OK

After enabling the trigger pulse option, the 'Start' button has to be clicked. The program will go through pretreatment and equilibration and will then wait for the trigger-signal.

Rescale after measurement.

Enable or disable automatic rescaling directly after the measurement of a voltammogram.

Rescale during measurement

When this option is activated, the graph in the Data presentation window is rescaled when a measured data point is outside the boundaries of the plot.

Procedure name in Data presentation Window

With this option it is possible to print the procedure file name on the Data presentation window. This is useful to identify the graph when it is dumped on a printer.

Show all GPES files in File dialog box

If this option is activated, all files of all techniques are shown in the File dialog boxes of the File menu. The program will switch automatically to the appropriate method.

Window

The Window option allows the selection of windows which should be shown on the screen. The Tile option gives the default partitioning of the screen.
The Close all option will delete all the GPES windows except for the status bar and the GPES Manager window.

Help

The Help option is the top entry point in the help structure. For most topics on the screen Help is available. By pressing F1 the specific information about the part of the screen on which has been focused is given.

Tool bar

The tool bar contains a list of buttons, the current electrochemical method, and the name of the current measurement procedure.
The buttons give short cuts to various menu options which are frequently used. Place the mouse pointer on top of a button. Its meaning will appear in yellow, if pressing the button is allowed.

3.2 Status bar

The lowest part of the screen is reserved for the status bar. The Start button starts the execution of a measurement procedure. After clicking this button, other buttons appear which allow to advance to a next stage or to abort a measurement procedure. The Status and Message panel give important control information.
After the Start button is clicked, the cell is switched on and the measurement starts with a pre-treatment.
If an automatic mercury drop electrode is connected to Autolab, the following control sequence is executed: the solution is purged, if the purge time exceeds 0 s. Subsequently a new drop will be created. Then the cell will be switched on and the pre-treatment potentials are applied when their duration is not zero. During these periods, the stirrer will be on. Before the measurement starts, the stirrer is switched off and the initial or standby potential is applied and the equilibration period starts in order to stop convection of the solution.

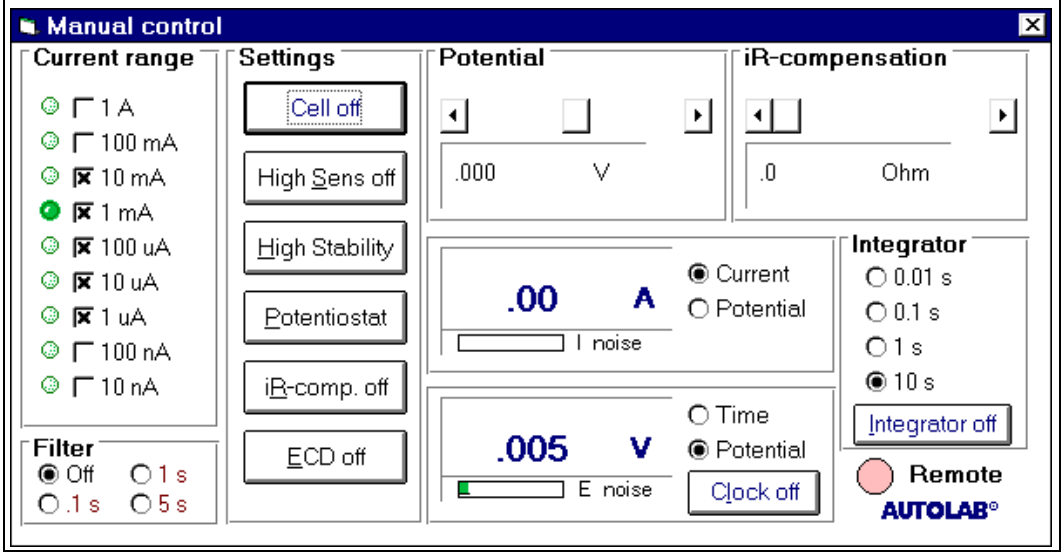
During the pre-treatment period, the measured dc-current is printed in the Manual control window.

3.3 Manual control window

The Manual control window gives full control over the potentiostat/galvanostat of the Autolab instrument, including the optional modules:

- the low current module ECD
- the bipotentiostat module BIPOT
- the 10 A current booster BSTR10A
- the integrator/filter module FI20 for the PGSTAT12/20/30/100.

Fig. 28 *Manual control window*



It is also possible to perform potential/current/charge measurements as a function of time. Note that some of the Autolab settings are part of the measurement procedure. The Manual control window consists of several panels.

Current range

In the Current range panel the green 'LED' indicates the actual current range. A mark in the neighbouring check box indicates whether the current range can be selected. Only a joined column of selectable current ranges is allowed. The software always checks whether the row is closed. If a range separated from another range is checked, the intermediate ranges are checked automatically. When a check box is clicked again, the check disappears. The allowed current ranges are stored on disk as part of the procedure. Sometimes a current range annotation is coloured red. This means that it is advised not to select this current range during execution of the current procedure. The response times of this current range is too high for the specified measurement procedure.

Settings

In the Settings panel, the mode of operation can be defined.The text on the button represents the current situation. The following buttons might appear (depending on the type of potentiostat/galvanostat):
Cell on/off: allows to switch cell on or off. In the ‘off’ position the connection of the potentiostat with the potentiostat/galvanostat is broken, so no current can flow between the counter and working electrode.
High Sens off/on: it indicates whether the gain 100 of the amplifier of the AD-converter is used. If "off" only gain 1 and 10 are used.
The current resolution is improved by a factor of 10. The disadvantage of the high sensitivity "on" is that the measurements are somewhat slower and that they are more susceptible to overloads. It is recommended to switch the high sensitivity "on" only when the limits of the digital resolution show. For example, at the current range 100nA the current resolution is improved from 3pA to 0.3 pA, when high sensitivity is switched on. See also the chapter about the digital base of Autolab in the "Installation and Diagnostics" guide.
High Stability/High Speed: The potentiostats/galvanostats can be used in either the high speed, with high bandwidth, mode or the high stability, with low bandwidth, mode. The bandwidth at high stability is about 10 kHz. Some electrochemical cells may cause stability problems with the instrument in high speed mode. Especially cells with high capacity and low resistance may cause oscillations. Using the instrument in high stability mode may prevent oscillations. It is advised to use high stability in all experiments, except when high bandwidth is needed. High speed or high bandwidth is needed when frequencies higher than 10 kHz or sampling or interval times below 100 µs are used.
Potentiostat/Galvanostat: allows switching from potentiostatic to galvanostatic mode. It is highly recommended to switch the cell off before the mode change. In case of potentiostatic control, the output of the DAC module corresponds to an applied potential level. In case of galvanostatic control, the output of the DAC module corresponds to an applied current.

iR-comp. on/off: switches iR-compensation' on' or 'off'. A more elaborate description is found in the dedicated paragraph in this chapter (only available with a PGSTAT12/20/30/100).

Potential

The Potential panel contains a slider and a text box. With these tools the applied potential can be specified. The slider box can be dragged to change the value. A click on the arrows and slider bar changes the value by a distinct increment. The increment is different for the arrows and for the bar.
In the two panels below the measured current, potential and/or time can be displayed, depending on the option button selected.
The option button "2nd Sig." appears, in case a chronomethod or the method cyclic or linear sweep voltammetry is selected and the Record second signal option is checked on page 2 of the procedure parameter list.
The Clock off/on button in the lowest of the two panels starts the timer, and displays the measured data from the panel above in the Data presentation window. This makes it possible to display graphically what is going on. These measured data can be replotted, printed, and the graph can be stored. However, the data can neither be saved, analysed, nor edited.

Noise meters

The noise levels for current and potential signals are visualised by 2 noise meters at the signal panels. When these VU-meters are active, the first green LED or a grey background is shown.
The VU-meter for the current signal is only active when the cell is switched on. The VU-meter for the potential signal is also active when the cell is switched off i.e. no current can flow. During the execution of the procedure (except for pre-treatment stage) the VU-meters are inactive.
In case more than 4 LED's of the VU-meter are on, it is advised to take precautions. You can select a higher current range or minimise the noise of your electrochemical cell. High potential noise levels are often caused by the reference electrode.

iR-compensation

The iR-compensation panel appears only when the Autolab is equipped with a PGSTAT12/20/30/100 potentiostat/galvanostat. In order to perform iR-compensation the iR-compensation button on the Settings panel should be switched to "iR-comp. on". Subsequently the Ohmic resistance can be specified using the slider or by typing in the textbox. Note that when the iR-compensation is switched on, automatic current ranging is no longer possible. The checked current range box becomes the actual current range.
In case of a manual change of the current range, the compensated resistance will be kept as constant as possible. Because internally the compensation is proportional to the current range, the value for the compensation needs to be recalculated when the current range is changed. With a change of current range the resolution of the compensation will alter. The maximum compensation of a current range equals two times the measurement resistance. This means that for the 1 A range the maximum

compensated resistance is 2 Ohm and for the 1 µA range it is 2 MOhm. The resolution is always 0.05% of the measurement resistance.

Integrator

The Integrator panel appears only when the Autolab is equipped with an analog integrator. This is not the case with a PGSTAT12/20/30/100 potentiostat/galvanostat unless the Autolab is equipped with a FI20-module. For further use, see the section about chronocoulometry.

Filter panel

The Filter panel appears when the Autolab is equipped with an ECD or an FI20 module. The following option buttons can be clicked "Off", "5s", "1s", ".1s". The effect of a filter constant of e.g. 5s is that 5 seconds after a potential perturbation has been applied, the current response can be measured correctly.

The “Remote led” indicates when it is possible to edit the parameters in Manual Control. In cases where it is red, it is not possible to edit the parameters in this window.

3.4 Data presentation window

The Data presentation window serves several functions:

- display of data
- data analysis
- data manipulation
- communication with other programs like Paintbrush, Excel or MS-Word.

The window consists of a menu bar, a graphical display, and a message line.
As mentioned earlier the measured data are kept in a shared data memory block with the data acquisition software. During the measurement the measured data points are also copied to the memory block of the Data presentation window. After the measurements the data in this memory block can be modified by options in the Data presentation window. However, it is always possible to resume the measured data. Note that the save options of the File menu of the GPES Manager window always save the measured data. Also note that for cyclic and linear sweep voltammetry, during the execution of a procedure, the measured data are plotted, but after the measurements only the last measured scan is visible. The data, which can be modified in the Data presentation window, are called work data and can be stored from the File menu of the Data presentation window in a work data file. This file cannot be distinguished from the files with measured data. Both types of files have the same format and layout. Some care should be taken with saving the work data. For example, as is described further on, the display of the current values can be changed to a square root of the current. If the work data are then saved, not the current values but the square root of the current is saved.

On the message line at the bottom of the graphical display important text about the required user actions during analysis of editing data appears. If no message is displayed, the currently measured potential and current are displayed.

File

The file option allows to create data files based op on data presented in the Data presentation window. It allows to save the so-called work data file as discussed above. The following options are available.

Save work file

This option was discussed above.

Save I(forward) and Save I(backward)

The Electrochemical techniques Square wave, Differential pulse and Differential Normal pulse provides the forward and backward current data. These curves can be plotted but not analysed. The separate curves can be stored, and retrieved with ‘File’, ‘Load data’ from the Gpes manager window to do analysis.

Save impedance data

When an AC voltammetry measurement is done, the impedance data for each data point can be saved to disk. This option is present in the File menu of the Data presentation window. The file, with the extension .IMP, has the following layout:

```
Date: 02-May-97
Time: 13:24:39
Frequency (Hz)  : 252.020
Amplitude (Vrms): .001
Phase sensitive : Yes
Phase (degree)  : 20.000
 E/V          i(ac)/A                Z/ohm       phi/deg    Rs/ohm      Cs/F
  .
  .
  .
```

NOTE: These data are additional data and can only be obtained after the measurement, NOT after loading a data file.

Quick save of previous scan

When a Cyclic or Linear sweep voltammetry measurement with more than one scan is going on it is possible to save the previous measured scan. This option can also be activated by typing 'SAVE' on the keyboard. This option work similar to the procedure parameter ‘Save every nth cycle’.

Save as Chrono data

Save a Step segment of Steps and Sweeps as Chrono methods data. This data file can be read in Chrono methods in order to perform data analysis.

Save as Linear sweep data

Save a Sweep segment of Steps and Sweeps as Linear sweep data. This data file can be read in the Linear sweep method in order to perform data analysis.

Copy

The Copy option allows to copy the graph to clipboard or to dump the graph in a bitmap file (.BMP). These files can be read by programs like Paintbrush, Excel or MS-Word. These programs allow editing of the graphs. The best result is obtained by doing this from a maximised Data presentation window. By default GPES only draws dots. It is sometimes better to draw lines. This can be achieved by double-clicking the data points in the graph. For further information, see the paragraph on Editing graphical items.

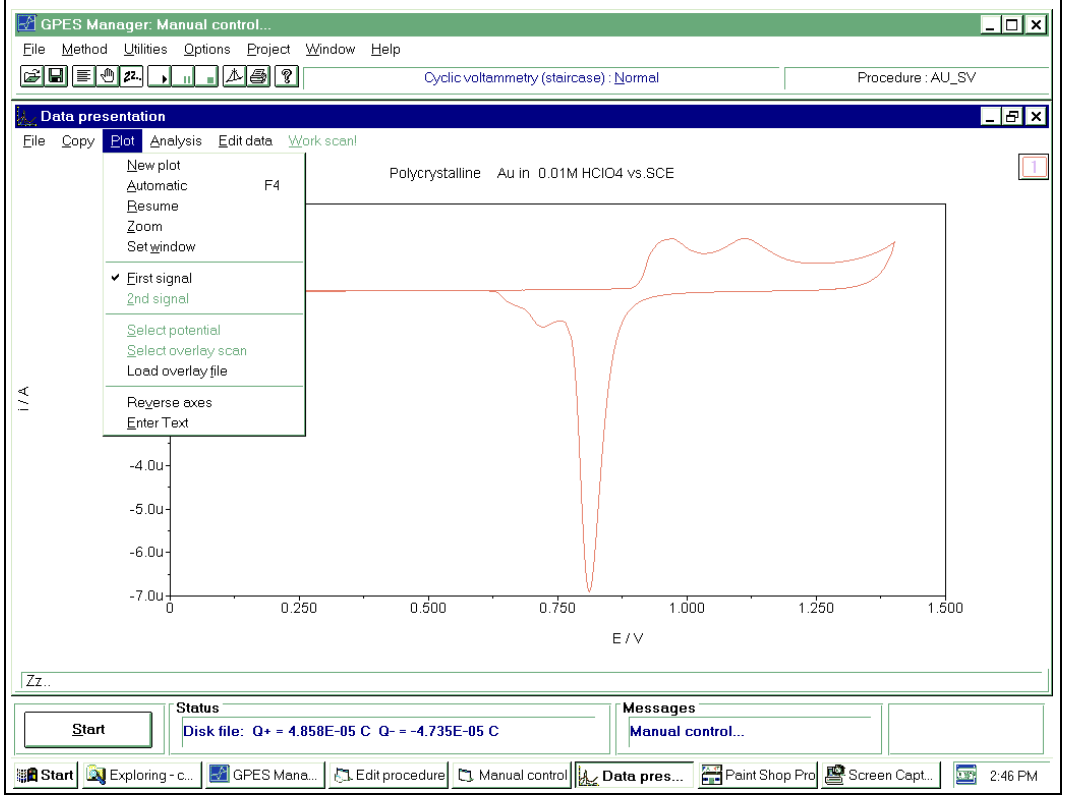
Plot

The Plot option contains all kind of possibilities to manipulate the graph like plot refresh, automatic scaling, zooming, setting a Data window, display of a previously measured signal. Sometimes, not all options are selectable because they are not applicable or intervene with current active data analysis options. Also when the execution of a procedure is going on, not all options are selectable.

New plot

The New plot option removes objects, such as lines and markers, from the screen. During measuring a cv, this option removes the previous measured data points from the screen.

Fig. 29 *The Plot menu*



Some sub-options require explanation.

Automatic

This option automatically rescales the data during a measurement.

Resume

The Resume option makes a fresh copy of the measured data into the Data presentation window. This allows you to get back to the original data after doing data analysis.

Zoom

Clicking the Zoom option has the same effect as pressing the right mouse button. When this option is activated a magnifying glass appears. When subsequently the left mouse button is clicked and held down a Zoom window can be created.

Set window

The Set window option allows to define a part of the data set. Any further data manipulation and display will be applied to this part of the data. With Chrono methods the x-values will be normalised to 0, so the x-axis always starts at t=0.

First- and Second signal

The First, and Second signal options are selectable, when, next to the current or potential signal, a second signal is recorded. A marker in front of these options means that they are displayed. When both are displayed no further data analysis is possible.

E vs t plot and dt/dE vs E plot

These options appear only when the method is Potentiometric stripping analysis. It allows switching between these types of plots. The E vs t plot can be used to do Transition time analysis (see the chapter on the analysis of measured data) in order to analyse the kinetics and reversibility of the electrode process. The dt/dE vs E plot can be used for electroanalytical purposes.

Show I (forward)

This option shows for the techniques square wave and differential pulse voltammetry only. With square wave voltammetry it allows to toggle the display of the current measured in the pulse which is applied in the scan direction. With differential pulse voltammetry it allows to toggle the display of the current before applying the pulse.

Show I (backward)

This option shows for the techniques square wave and differential pulse voltammetry only. With square wave voltammetry it allows to toggle the display of the current measured in the pulse which is applied in the opposite of the scan direction. With differential pulse voltammetry it allows to toggle the display of the current measured in the pulse.

Load overlay file

This option allows the making of a graphical overlay of one or more data sets. A maximum of 10 overlays can be made. You can select multiple files at a time by using <Shift> or <Control>, combined with the mouse action.
The overlay legends shown in the Data presentation window, will also be visible in a print-out. After clicking the New plot option or the Resume option, the overlays will disappear. It is possible to load overlays together with the main data (see Load data/scan option of the File menu)

Reverse axes

This option will reverse the direction of the horizontal as well as the vertical axis. It allows peaks always to be displayed upwards.

Enter text

When this option is clicked the text "Text field" appears in the left top corner of the graph. This text can be dragged over the graph. After double-clicking the text field, the text itself, and the format can be modified. The first text line of the Paste buffer can be inserted on the text field as well. Thus a line of text from the Analysis results window can be copied to the Paste buffer and subsequently inserted there. Please note, that the text cannot be stored.

Analysis

The Analysis option contains an elaborate set of methods to extract essential parameters from the measured data. The background is described in the special chapter about this subject. The available data analysis options depend on the selected electrochemical method.

Edit data

The Edit data option gives the opportunity to modify the presented data. The backgrounds are explained in the special chapter about this subject.

Work scan

The Work scan option, which is only present for cyclic and linear sweep voltammetry, allows the selection of a scan for further data analysis.

Work potential

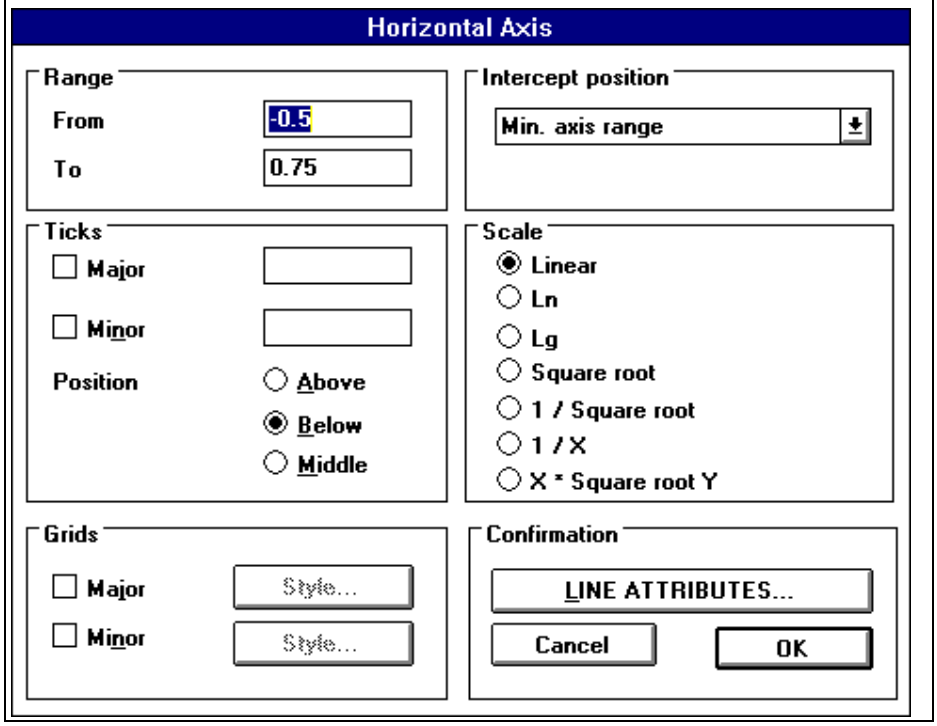
The Work potential option, which is only present for multi mode electrochemical detection, allows the selection of a potential for further data analysis and peak search.

Editing graphical items and viewing data

Except for the available options, items of the graph can be edited by double-clicking them. The following items can be double-clicked:

- the axis annotation
- the axis itself

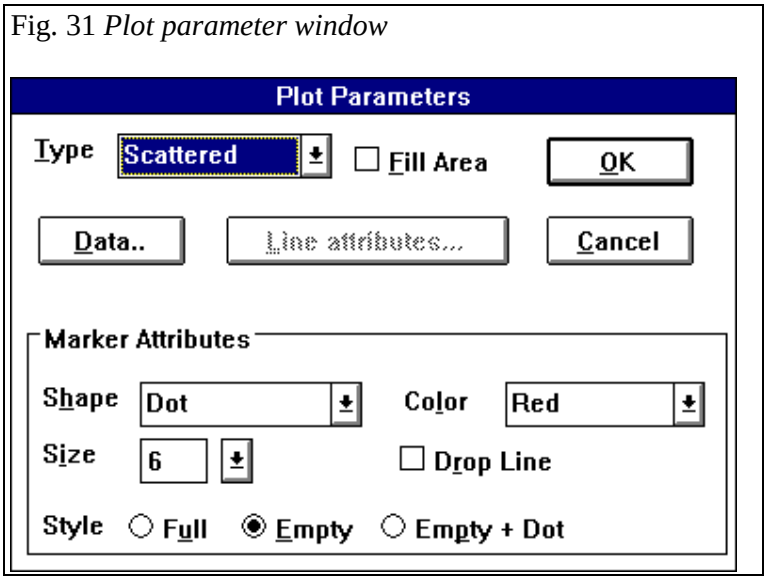
Fig. 30 *Horizontal axis window*



- the axis description
- the plot title and subtitle
- the data.

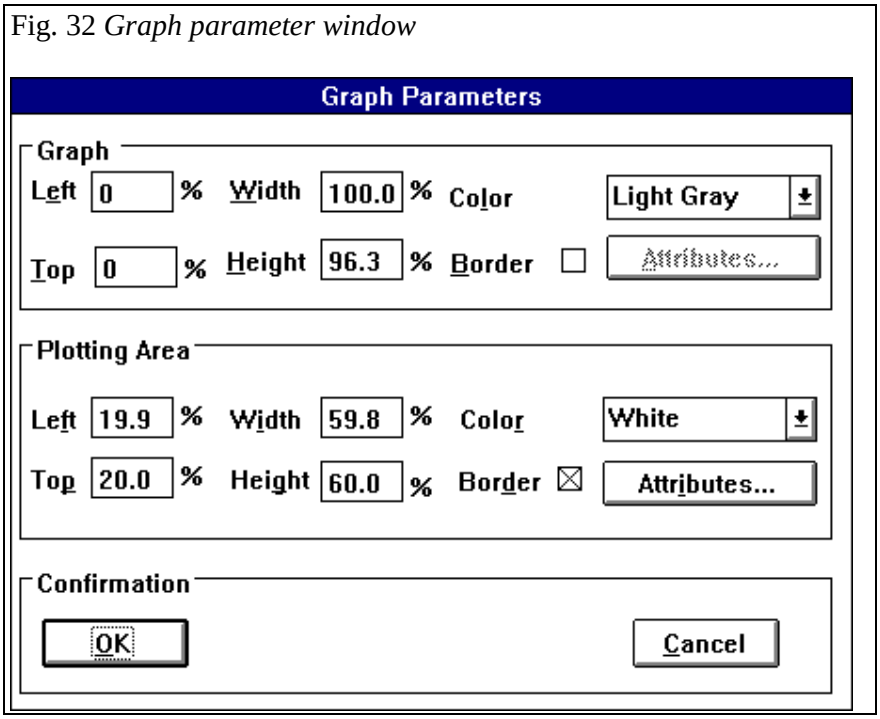
Colours, sizes, marker types, text, formats, axis position: all these things can be changed. Please take some care with changes in Colours. E.g. do not make the data colour the same as its background colour.

Fig. 31 *Plot parameter window*



By double-clicking the data points a window appears, which among the standard graphical operations also gives the possibility to view the data values itself and to edit them. Moreover the data can be copied to clipboard and subsequently be entered into e.g. a spreadsheet program.

Fig. 32 *Graph parameter window*



Double-clicking the axis itself allows scaling and positioning of the axis and selection of the axis function. Data can be displayed, among others, as linear inverse, ^{10}log, natural log, square root, inverse square root. Except for the linear and ^{10}log, the value

of the presented data is modified in real. So all subsequent operations are really performed on e.g. the square root of the data.
In case of the ^{10}log, not the values but the axis is changed to a logarithmic axis.

When the button "| 1 |" in the upper right corner is clicked, the Graph parameter window appears. This window allows modification of the relative scale parameters of the so called graph and plotting area, and their background colours.

All the changes made to colour and sizes are stored in the default graphics display file. The other changes are kept in the procedure file.

3.5 Edit procedure window

The Edit procedure window consists of 2 pages. In Page 1 the most common parameters can be specified. Page 2 contains the other parameters. The meaning of each parameter is clarified by the Help program.
A list of parameter descriptions is given in the appendix about this subject.
In the option bar, the Send option is displayed. This option can only be clicked during the execution of a measurement procedure. It is relevant when a parameter is changed. The Send option activates the modified value. The modified value is accepted when a beep sounds.
The layout and setup of the Edit procedure window is more or less the same for all electrochemical methods.

For most methods on Page 1, the following type of parameters can be specified:
- the first pre-treatment and subsequent equilibration
- the definition of the type of measurement
- the potential or current level parameters
- the title and subtitle.

The items on page 2 depend on the method.

For voltammetric analysis the following extra items are available:
- number of voltammetric scans which will be recorded subsequently and averaged
- a number of comment lines.

For cyclic and linear sweep voltammetry the following items are extra available:
- extra pre-treatment stages
- special measurement conditions
- special display option to swap x- and y-axis (Tafel plot)
- a number of comment lines
- current boundaries for reversing the scan direction
- optional chronoamperometric measurement conditions at the vertices
- optional recording of an external signal.

For the chronomethods the following extra items are available:
- extra pre-treatment stages
- special measurement conditions

- optional recording of an extra signal
- a number of comment lines.

For electrochemical detection the following extra items are available:
- extra pre-treatment stages
- a number of comment lines
- differential pulse condition (if applicable).

For potentiometric stripping analysis the following extra items are available:
- smooth level during differentiation of potential versus time data
- a number of comment lines.

A full list of input parameters is given in appendix II.

3.6 Analysis results window

The Analysis option of the Data presentation window allows the making of an analysis of the data. In some cases the results are displayed in a special window which differs per analysis technique. In all cases a report of analysis is printed in the Analysis results window.
The Analysis results window contains all the results of the analysis of the data. Only when the GPES Manager window is closed, the Analysis results window is cleared. The File option of this window allows the user to clear, save or print the content of the window. The Edit option allows the user to remove (Cut) the selected part of the text. Text can be selected by keeping the left mouse button pressed and moving it over the window. The Copy option copies the content of the window to the paste buffer including a so called DDE link. For example, MS-Word can, via Paste special option makes a Paste Link. This means that any change to the content of the window will automatically be copied to the MS-Word document until the link is broken via the Links... option of MS-Word.
The Paste option will include text from the paste buffer.

It is possible to copy results of Analysis into the graph of the Data presentation window. This is useful if you want to have a complete printout of the graph. You can include the Analysis text as follows:
- You can select (a part of) the text,
- Under the option Edit click the option Copy (or Cut). Now the text is present in the paste buffer,
- Now select the Copy menu on the Data presentation window,
- Select Paste text.

The text will be included into the graph.

Please note:
In the Data presentation, you can drag the text to the position you want. The text in Data presentation can not be changed, but can be cleared by double clicking and typing in a space in the Text field. You can also change the text style in the window. For a proper outlined text a change to the font ‘Courier’ is sometimes required.

4. Analysis of measured data

Under the Analysis option on the Data presentation menu there are a number of facilities to analyse measured data. Some analysis techniques are specific for an electrochemical method.
The results of the analysis are sometimes displayed in a specific window. In all cases the results are printed in the Analysis results window. This window can be made visible from the Window option on GPES Manager menu bar.
In most cases not all options are selectable. This may have the following causes:

- The option is not relevant for the electrochemical method.
- The execution of a measurement procedure is in progress.
- Another conflicting option is already selected.
- Just after the recording of more than one cyclic or linear sweep voltammogram, a selection of the scan to be analysed can be made. See Work scan option on the Data presentation window. By default the last measured full scan is displayed.
- When a second signal has been recorded concurrent, first a selection has to be made which signal should be analysed. See Plot menu on the Data presentation window.
- The option is not relevant or cannot activated because an ambiguous situation is present, i.e. it is not clear on what data the analysis should be done.

4.1 Peak search

When the Peak search option is selected, the Peak search window appears. If the curve shows distinct peaks, you can often simply click the Search button in the right panel and the results are shown in an appearing Results panel. The number of digits is the same as the precision of the axis.
The Clear button will erase the Results window and will refresh the plot. The Close button closes the Peak search window. The Show results button will show the Results window.
The Peak search options window gives several options to search for peaks in a voltammogram. It opens when the Option button is clicked. If Automatic option button is 'checked', the peak search algorithm needs two input parameters to be specified: the minimum peak height and the peak width. Otherwise only a value for the minimum peak height is required. These parameters have to be specified in the Minimum panel. Peaks with a height below the minimum peak height will be omitted. The peak width parameter determines the width of the window which moves through the data set. Peaks with a width (at half peak height) which are smaller than the specified peak width might not be found.
It is possible to find peaks that are present as shoulders on a steep base curve.
For this purpose the Peak search option contains an Include shoulders option. The option is found at the Peak search options window and can be selected only in automatic search mode.
When this option is clicked on, the Peak search is performed after a basecurve correction on the background, according to the moving average baseline correction

method. This method can also be performed separately. See Baseline correction option in the Edit data menu.

Fig. 42 *Peak search window*

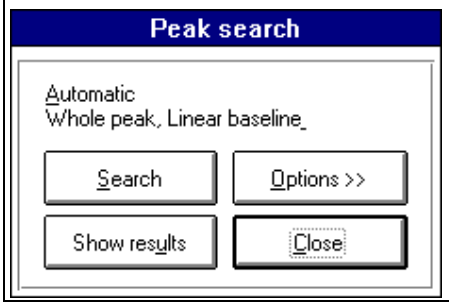


Fig. 43 *Peak search options window*

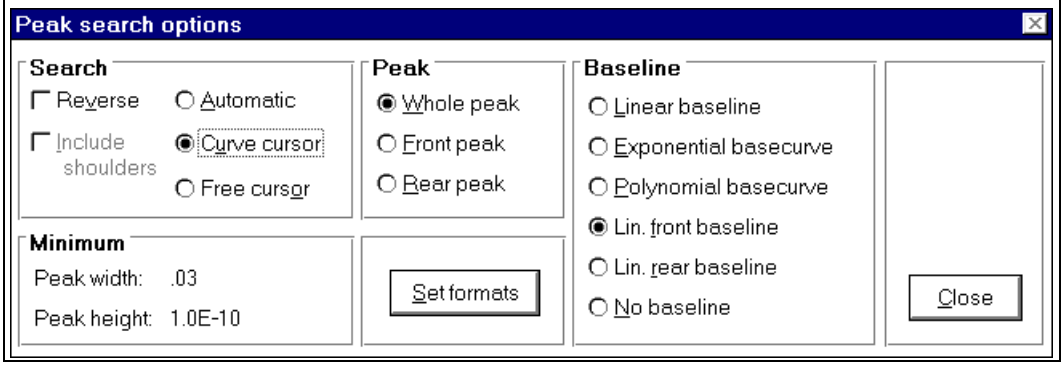


Fig. 44 *Set results format window*

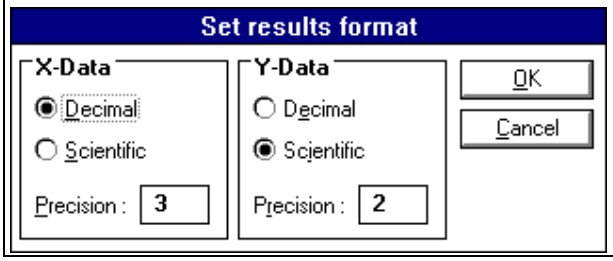
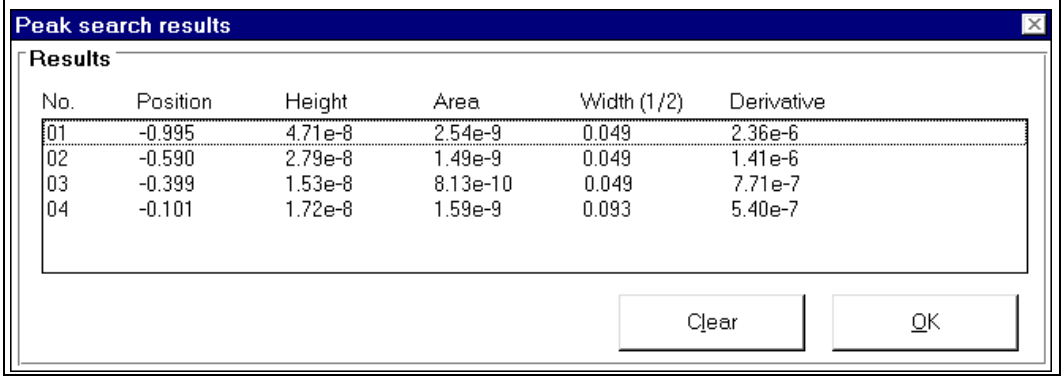
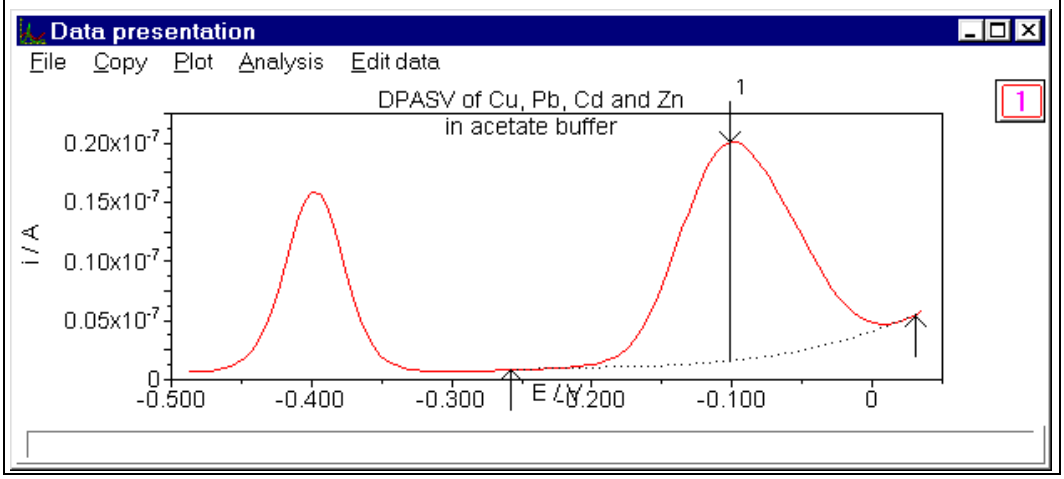


Fig. 45 *Peak search results window*



Peaks are normally searched in the scan direction. If this is not required, the Reverse option in the upper right corner of the window should be checked.
In the Baseline panel it can be 'checked' whether or not the peaks found will be corrected for the baseline. This baseline is determined by means of the tangent fit method.
The tangent is drawn from the left side to the right side of a peak if ‘linear baseline is checked’. In cyclic and linear sweeps it may be better to use only the front of the peak to construct the tangent. This is done when ‘Lin. front baseline’ is checked.
If the automatic peak search method fails, the Automatic search should be switched off. Two alternatives are present: curve cursor and free cursor. In both modes two points need to be marked; the beginning and the end point of the peak. In curve cursor mode the markers are automatically put on the voltammogram. In free cursor mode the marks can be put everywhere on the graph. In curve cursor mode the two markers several types of basecurves can be drawn: linear, 3rd order polynomial, or exponential. Moreover, in case of double peaks, only peakheight of the front peak, the rear peak, or highest in the whole selected peak area can be determined.

Fig. 46 *Example of polynomial basecurve in peak*

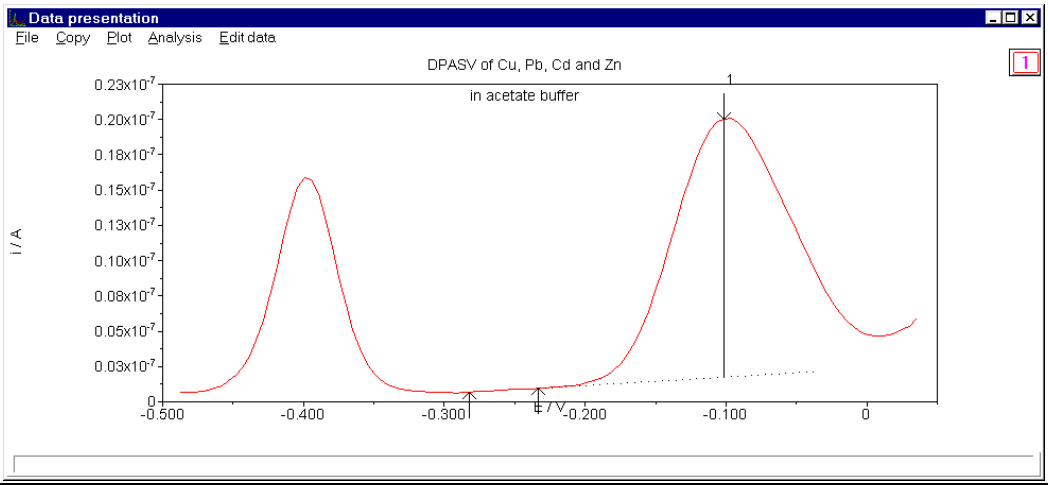


Furthermore it is also possible to draw a linear baseline in case only the front part or only the rear part of the baseline is known. The options Lin. front baseline or Lin. rear baseline on the Baseline panel should then be ‘checked’. Now two points on the front part respectively rear part of the peak should be marked. In free cursor mode only a linear baseline can be drawn.
When the options 'Curve cursor, linear baseline' and 'Free cursor' are selected, baselines can be constructed manually. After the first point of the baseline has been marked, a line connected to this point will be dragged until a second marker is clicked.
The Set format button can be clicked to adjust the formats in the Set results format window. The defaults in this window are the formats of the axis-labels.

The results of the peak search are:

Position : potential at which the current with respect to the baseline has a maximum.
Height : maximum current with respect to baseline.

Fig. 47 *Example of a linear front baseline*



Peak area : area of the peak corrected for the baseline. For data from cyclic linear sweep voltammetry the area is expressed in Coulombs. This means that the area is divided by the scanrate.
Derivative : the sum of the absolute values of the maximum and the minimum in the derivative of peak.
Ep - Ep/2 : the difference between peak potential and the potential at half height. This value is only printed for data from cyclic and linear sweep voltammetry. It is useful to derive kinetic parameters. See the book of C.M.A. Brett and A.M.O. Oliveira Brett, Electrochemistry Oxford science publications ISBN 0-19-855388-9.

In quantitative voltammetric practice the peak height is the most widely used parameter to determine concentrations. The peak area is less sensitive to noise, but if the peak is not completely isolated from another peak, the error in the peak area will be high. The sum of the derivatives of the peak is less sensitive to peak overlap. However, derivation of an experimental curve will increase noise. For more details see Ref.: J. Tacussel, P. Lectere and J.J. Fombon, J. Electroanal. Chem.,214 (1986) 79-94.

4.2 Chronoamperometric plot

The Chronoamperometric plot option produces a special plot for two sequential potential steps in a chronoamperometric experiment. The first step should be the forward potential step and the second the reverse potential step in a (quasi-)reversible electrode reaction. The book of A.J. Bard and L.J. Faulkner, Electrochemical Methods, Fundamentals and Applications, Chapter 5 (ISBN 0-471-05542-5) gives more details.
If data for more than two potential steps are present, a selection of the first (forward) potential step can be made. This option is only active if it is applicable.

4.3 Chronocoulometric plot

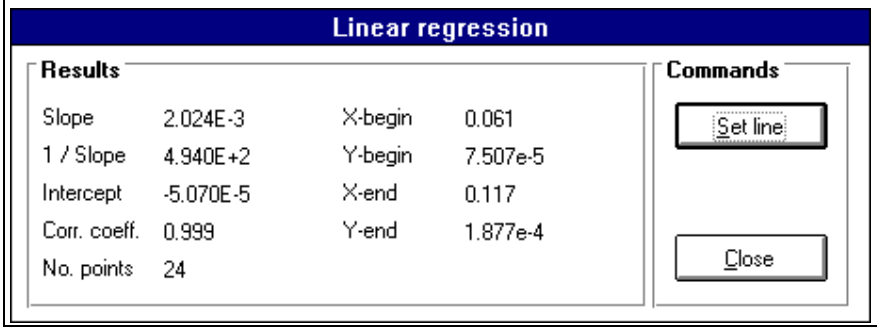
The Chronocoulometric plot option produces a special plot for two sequential potential steps in a chronocoulometric experiment. The first step should be the forward potential step and the second the reverse potential step in a (quasi-) reversible electrode reaction. The book of A.J. Bard and L.J. Faulkner, Electrochemical Methods, Fundamentals and Applications, Chapter 5 (ISBN 0-471-05542-5) gives more details. If data for more than two potential steps are present, a selection of the first (forward) potential step can be made. This option is only active if it is applicable.

The charge flown since the beginning of the potential step is plotted versus the square root of the time since the start of the step.
The kinetic parameters can be obtained by selecting the Linear regression option (see below). A line should be fitted for the forward as well as for the reverse plot. The fit parameters appear in the Analysis results window as well as in the results panel.

4.4 Linear regression

The Linear regression option allows to fit a straight line through a part of the measured curve.
When the option has been selected, two windows appear. One is the Linear regression window and the other is the Markers window. When the user has marked the begin and end point of the line on the measured curve and has clicked the OK button, a line is drawn so that the sum of squares of the differences between measured and calculated value is minimum.

Fig. 48 *Linear regression window*



The slope of the line (dY/dX), its inverse, the intercept (the value at X = 0), the number of points between begin and end point, the standard deviations and the correlation coefficient are displayed in the Linear regression window. More lines can be fitted when the Set line button is clicked.

4.5 Integrate between markers

This operation will determine the area under the curve between two selected points. With cyclic voltammetry, the area is expressed as charge (C). Thus the calculated area is divided by scanrate.

4.6 Wave log analysis

The Wave log analysis option is active for voltammetric analysis and cyclic and linear sweep voltammetry.
The half wave potential $E_{½}$ can be determined and Tafel slope analysis can be done for a S-shaped cyclic voltammograms or convoluted voltammograms (see Convolution option). After having selected this option, the user is asked to define a base line and a limiting line. Subsequently $E_{½}$ is calculated from the crossing between the average line of the base line and the limiting line with the measured curve. The limiting current at $E_{½}$ is calculated as two times the current at $E_{½}$ with respect to the base current.
After pressing the Continue button on the Wave log analysis window, a Tafel line analysis can be done from the plot of ln {(id - i)/i} versus the potential, where "i" stands for current, "id" for limiting current and "ln" for natural logarithm. If a cyclic voltammogram has been deconvoluted the "i" is replaced by "m". The markers for the line should be selected not too far from zero on the Y-axis.
The intercept is at E = 0. The parameter Alpha * n (αn) has been calculated from the slope:

slope = αnF/RT

F = Faraday constant = 96484.6 C/mol
R = Gas constant = 8.31441 J/mol/K
T = temperature = 298.15 at 25°C
n = no. of transferred electrons
α = 1 for reversible reactions
α = transfer coefficient for irreversible reactions.

An example of wave log analysis is described in Chapter 'Getting started with GPES'.

4.7 Tafel slope analysis

This option is only available for Cyclic and Linear sweep voltammetry. When the option is selected, the current is plotted on a logarithmic scale. The user is asked to set markers for the anodic and cathodic branch on the curve. In principle this option works similar to Corrosion rate analysis without the fitting part.

4.8 Corrosion rate

This option allows the determination of the corrosion rate and the polarisation resistance.

If the current versus the potential curve passes the zero current line more than once, the user is asked to define a window of interest around the point where the anodic current balances the cathodic current. Before doing this, it might be useful to draw the horizontal axis through the origin of the vertical axis. This can be done by double-clicking the horizontal axis and subsequently selecting the "Origin" in the Intercept position panel.
If the curve passes the zero current line only once, the whole curve is used for the analysis.

Subsequently the graph is transformed in a logarithmic scaled current versus potential plot and the Corrosion rate window appears. This window shows the corrosion potential and the polarisation resistance at the corrosion potential.
In this window the surface area (SA), equivalent weight (EW), and the density (D) of the electrode material can be specified. These data are used to calculate the corrosion rate in terms of current density ($I_{corrosion}$) and millimetres/year (CR):

$I_{corrosion} = i_{corrosion} / SA$ A/cm2
and
$CR = 3272 * i_{corr} * EW/(SA * D)$

The polarisation resistance Rp is determined by taking the reciprocal value of the derivative di/dE. The derivative is obtained from a 2nd order polynomial fit through the corrosion potential and its neighbours. From this Rp value the corrosion rate can be obtained:

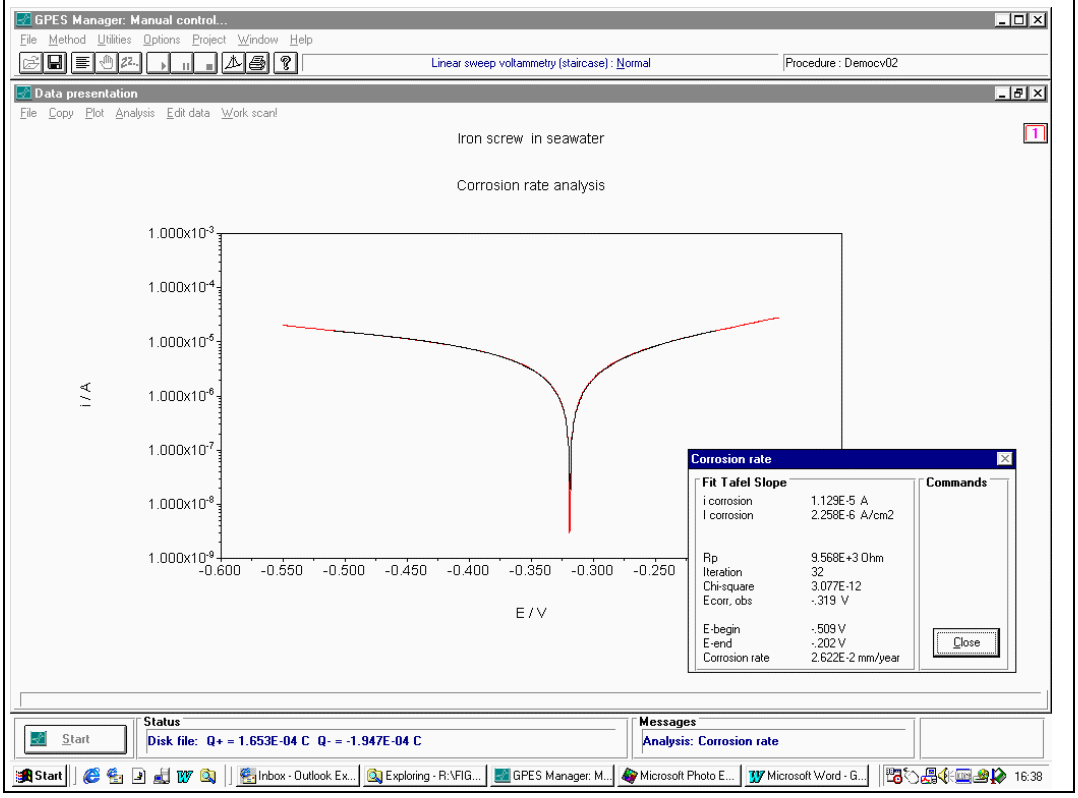
$i_{corrosion}$ = B/Rp where B is normally an empirical constant.
B can also be obtained from the Tafel slopes (M. Stern and A.L. Geary, J. electrochem. Soc. 1957, 104, 56).

After clicking the Tafel slope button, the Marker window appears. Now the Tafel line for cathodic branch has to be defined by marking two points. After the OK-button on Marker window has been clicked, the same has to be done for the anodic branch. After the Tafel lines have been set, a second Corrosion window appears with the results:

1. The corrosion current, corrosion current density and the corrosion rate.
2. The Tafel slopes b_a and b_c.
3. The corrosion potential at zero current and the corrosion potential as calculated from cross-point of the two Tafel lines.
4. The Polarisation resistance Rp obtained from the equation:

$$Rp = B/i_{corrosion} \text{ where } B = \frac{1}{S} \quad \text{and } S = 2.303 * \left(\frac{1}{b_a} + \frac{1}{b_c} \right)$$

Fig. 49 *Corrosion rate analysis*



The corrosion rate is determined on the basis of the equation:

$$i = i_{corrosion} \left\{ \exp\left[s1(E - E_{corr}) \right] - \exp\left[-s2(E - E_{corr}) \right] \right\}$$

where s1 = slope of the anodic branch = $2.303/b_a$
s2 = slope of the cathodic branch = $2.303/b_c$
E_{eq} = the equivalence or corrosion potential
$i_{corrosion}$ = the corrosion rate or exchange current in Ampere

When the Start fit button is clicked, a fit is performed on the slopes and the corrosion current. The observed corrosion potential, i.e. the potential where i = 0, is taken as the corrosion potential E_{corr}.
The fitting is performed according to the non-linear least square fit method of Levenberg/Marquardt. The values obtained from the Tafel lines are used as start parameters. After some iterations the fit results are presented on the screen. Also the number of iterations and the goodness of fit parameter chi-square are given. Chi-square is the sum of the squares of the differences between measured and calculated data. The fitted slopes are s1 and s2. The fitting procedure can be interrupted by clicking the Stop button.
The comparison between the observed and the calculated curve is shown.

The Tafel slope parameter α can be obtained from the slopes:

$b = 2.303\ RT/3\alpha nF$

F = Faraday constant = 96484.6 C/mol
R = Gas constant = 8.31441 J/mol/K
T = temperature = 298.15 at 25°C
n = no. of transferred electrons
2.303 = ln (10)

It is sometimes possible to improve the fit by clicking the Restart button.

4.9 Spectral noise analysis

After recording current- and potential- noise transients, it is commonly desired to perform a statistical or frequency analysis on the results. The GPES software enables the calculation of a frequency spectrum for current and potential or impedance. It can be activated in the Analysis menu of the Data presentation window.
The frequency spectrum is calculated by means of a FFT algorithm. Since it requires the dataset to be a power of 2, the number of datapoints is automatically extended when necessary. In case of an interrupted measurement (<Abort> was pressed), the dataset is padded with zeros.
In principle, the Fourier method should only be used on datasets that are periodical and “fit” exactly in the time duration of the recorded scan. For noise signals, this is of course not true. Therefore for some cases, it would be advisable to apply a so-called

“Window function”. These operations will counteract the effects that were mentioned above. A total of 5 functions are available:
none/Bartlett/Hanning/Hamming/Blackman.
A range of literature is available on the theoretical background of signal processing.

See: “Numerical Recipes”, W.H.Press et al., Cambridge University Press, Cambridge 1997

4.10 Find minimum and maximum

The Find minimum and maximum option shows the minimum and maximum Y-value with their corresponding X-values.

4.11 Interpolate

The Interpolate option allows the user to calculate one or more X-values or Y-values which corresponds to a given value on the other axis. A linear interpolation is used to calculate intermediate values.

4.12 Transition time analysis

The Transition time analysis option only appears for chronopotentiometric data or data from Potentiometric stripping analysis. The background of this analysis is fully described in the book of C.M.A. Brett and A.M.O. Oliveira Brett, Electrochemistry Oxford science publications ISBN 0-19-855388-9.
After selecting this option, a graph of the time versus potential is presented and the user is asked to specify two marker points for subsequently the baseline, the transition line, and the limiting line.
The time difference between the crosspoints of the transition line and the base line respectively the limiting line is defined as the quantity 'tau'. The crosspoint of the transition line with the baseline is called t-base of 'tau'. Finally also the quantity E3/4 - E1/4 is given. This is the difference in potential at three quarters of 'tau' and at one quarter of 'tau'.
Subsequently the plot can be transformed dependent on whether the measured system is thought to be reversible or irreversible. Finally a linear regression can be done to extract the kinetic parameters from fitting a straight line. An example of transition time analysis is given in the chapter ‘Getting started with GPES’.

4.13 Fit and simulation

The Fit and simulation option is located in the Analysis menu of the Data Presentation window. It provides the method to determine parameters of electrochemical processes, like formal redox potential, heterogeneous rate constant, transfer coefficient α etc., as well as to simulate theoretical current-potential curves. The table

below summarises the models (i.e. combinations of experimental techniques and reaction mechanisms) for which fitting and simulation are currently available.
The models available for fitting and simulation are extended with the mechanisms in which two parallel reactions are involved. The models are called 'two-component' models and are available for the cyclic voltammetry technique.

Table 2 *Models available for fitting and simulation.*

staircase cyclic voltammetry	**differential pulse voltammetry**	**normal pulse voltammetry**	**square wave voltammetry**
reversible	reversible	reversible	reversible
quasi-reversible	quasi-reversible	quasi-reversible	quasi-reversible
irreversible	irreversible	irreversible	irreversible
ErCi (irreversible chemical reaction)	ErCi (irreversible chemical reaction)	ErCi (irreversible chemical reaction)	ErCi (irreversible chemical reaction)
two-component			

In all the above models it has been assumed that the experiment is carried out on a stationary electrode in an unstirred solution. The fit and simulation works only with staircase voltammograms but not with linear scans. Moreover, in cyclic voltammetry, the current measured during a potential step depends on the “history” of the scan, i.e., on the number, height and duration of all preceding steps. This means that for the sake of speed, the number of potential steps should in the scan should be kept small.

The simulation method

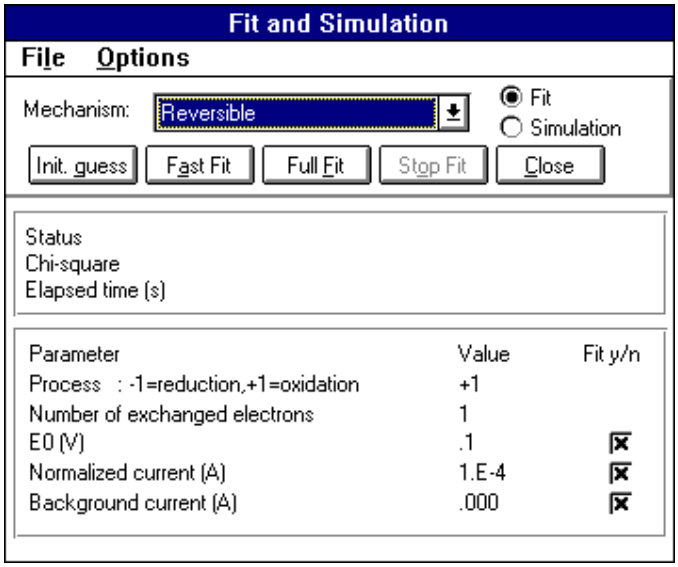
Digital simulation of current-potential curves is based on finite difference method. Equations of the transport of electroactive substances to the electrode surface are solved by Crank-Nicolson technique, a method widely used by electrochemists and renowned for its accuracy and stability. The time-dependent concentration profiles obtained from these equations are used for the calculation of the current.
The advantage of digital simulation is its versatility. This feature is easily visible when the simulation method is compared with analytical equations describing current-potential curves, which have a number of restrictions on their validity.

The fitting method

Fitting is carried out using Marquardt nonlinear least-squares method. The model functions are either calculated from analytical equations (wherever possible) or obtained by digital simulation of the electrode processes. The convergence criteria are based on the value of χ^2 , $\Sigma(Y-Y_{fit})^2$, and its change during the last iteration, as well as on the requested precision of the fitted parameters.

Elements of the Fit and Simulation Window

Fig. 50 *Fit and simulation window*



In the upper part of the Fit and simulation window there is the drop-down menu with a list of available models, five action buttons, and two option buttons to switch between the fit and the simulation mode of the program. The list of models that can be used depends on the experimental technique chosen.
The middle part of the window contains three display fields. 'Init. Guess' button starts the calculation of the initial guesses of fitable parameters. Fast Fit performs a fit on a reduced data set. See the chapter ‘Fitting in more detail’ about the data reduction and other fast fit parameters. The Full Fit button starts a fit of the model on all data points. This button is replaced by the Simulate button in case the simulation option is chosen. The Stop Fit button will interrupt a running fit procedure. Fields show the status of calculations, the value of χ^2 and the elapsed time.
The lower part of the fit and simulation window displays the parameters. Normally, only fitable parameters are shown (it is possible to display all parameters by choosing the Extended setup option from the Option menu). Each line contains the name of the parameter, its value and a checkbox to indicate whether the parameter should be fitted or not. In extended setup, in each line there are additional fields for the value and the type (absolute, relative or disabled) of the convergence criterion.

Fitting and simulation step by step

Fitting

1. Load a cyclic voltammogram file, C:\AUTOLAB\TESTDATA\DEMOCVO3.0CW.
2. From Analysis menu (Data presentation window) select Fit and Simulation.
3. Select the model 'reversible' from the drop-down menu in the top part of the appearing window.

4 Make sure the switch right to the model name is set to Fit.
5 Get the initial guesses for the parameters either by clicking Init. guess button, pressing Alt-G or by choosing Initial guess from the Option menu.
6 Check whether the number of exchanged electrons is correct.
7 Select parameters to fit by checking the boxes next to parameter names. If necessary, adjust the starting value of parameters by clicking it with the mouse pointer and entering the new value (make sure that the number of electrons is set to 2).
8 If necessary, switch to extended setup (Option menu, or Ctrl-E) to edit other parameters or to change parameter's convergence criteria. Parameters that are visible in the extended setup but invisible in the standard setup are not fitable, i.e., their values are not changed during the fit process (see "Fitting: choosing parameters to fit" and "Fitting: convergence criteria" for more detailed information).
9 Select Full Fit control parameters from the Option menu and adjust their values (see "Fitting: advanced options" for details).
10 Click Fast Fit button on a reduced number of data points.
11 The fitting proceeds until the convergence criteria are satisfied or the maximal number of iterations is reached, whatever comes first. It is possible to stop fitting at any moment by clicking Stop fit button. It is possible, that the program will need a few seconds to complete the iteration before stopping.
12 During the fit, the field Status shows the number of the iteration, field Chi-square shows the χ^2 value and field Elapsed time shows time elapsed from the start of the fit.
13 If convergence is reached, the Status field contains information "ready" and the number of iterations.
14 If the maximal number of iterations has been carried out without reaching the demanded convergence criteria values, the status field displays information "stopped" and the number of iterations.
15 If fit has been stopped by Stop fit button, the status field displays information "interrupted".
16 Pressing Full Fit starts the new cycle of fitting, taking all data into account, with as start values the values visible on the screen. The number of iterations and the elapsed time counter are reset.
17 Fit parameters can be saved using option Save fit parameters and reloaded using the option Load fit parameters (both options from File menu).
18 To replace the work data by the fitted curve use Make work data option from the File menu.
19 To quit the fit window click the Close button, press Alt-C or select Close from the File menu.

During fitting the results of each iteration are shown in the Data Presentation window together with the original data set. It is possible, that some iterations will go in the wrong direction delivering worse approximations than the previous one. In this case the fitting procedure steps back and tries to obtain another, better approximation. The process of stepping back can take few iterations, during which curves observed on the screen may differ severely with the analysed data. However, this is not a reason to worry, as the fitting procedure finally comes with a better approximation.

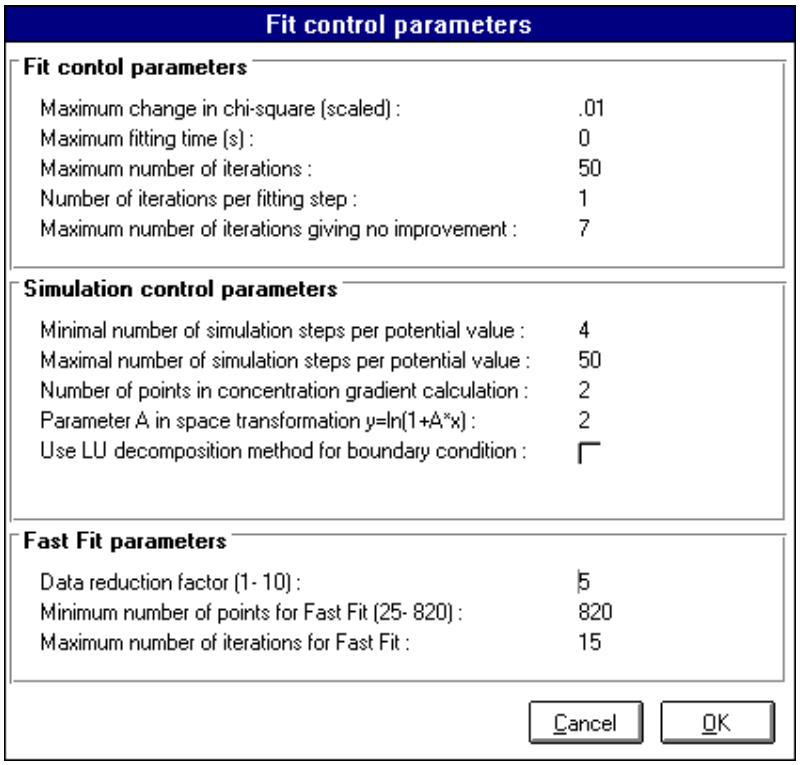
Simulation

1. Load the differential pulse voltammogram C:\autolab\testdata\demoea01.
2. Set a window (see Plot menu on Data presentation window) between -1.150 and -0.850.
3. From Analysis menu (Data presentation window) select Fit and Simulation.
4. Select the model reversible from the drop-down menu in the top part of the appearing window and set the simulation mode by activating radio-button Simulation.
5. Switch on extended setup (option Extended setup in the Option menu or Ctrl-E).
6. Set values of parameters.
7. Check whether the type of the process (oxidation/reduction) is set correctly.
8. Each parameter has its allowed range. If a value is entered that exceeds this range, it is automatically adjusted to fit within it.
9. If necessary, adjust simulation options (Fit control parameters in the Options menu). For details on these options see "Simulation: advanced options".
10. The Init. guess button can be used all the time to obtain estimates of parameters for the work data.
11. Press Simulation button or Alt-S to start calculations.
12. When simulation is completed, the status field shows message "simulation ready". The χ^2 field displays the sum of squares of datapoints values, $\sum_i y_i^2$.
13. The comparison can be improved by switching to ‘Fit’ and selecting ‘Full Fit’.

To make simulation results permanent, select the Make work data option from the File menu. Close the fit and simulation window (Close button or Alt-C or Close option from the File menu), or switch to fitting (by pressing Fit button close to the model name), or select another model. In the last case a new list of parameters appears with their default values.

Fitting: advanced options

Fig. 51 *The Fit control parameters*


Fit control parameters
Fit contol parameters
Maximum change in chi-square (scaled) : .01
Maximum fitting time (s) : 0
Maximum number of iterations : 50
Number of iterations per fitting step : 1
Maximum number of iterations giving no improvement : 7
Simulation control parameters
Minimal number of simulation steps per potential value : 4
Maximal number of simulation steps per potential value : 50
Number of points in concentration gradient calculation : 2
Parameter A in space transformation y=ln(1+A*x) : 2
Use LU decomposition method for boundary condition :
Fast Fit parameters
Data reduction factor (1- 10) : 5
Minimum number of points for Fast Fit (25- 820) : 820
Maximum number of iterations for Fast Fit : 15
Cancel
OK

It is possible to fine-tune the fitting process. Parameters influencing the fit can be set by choosing Fit control parameters (Option menu) or by pressing Ctrl-P. The following parameters appear on the screen:

Fit control parameters

Maximum change of chi-square (scaled):
The convergence is reached when the last change in χ^2 is not larger than the given fraction of χ^2 value.

Maximum fitting time:
The time limit of fit procedure. If it is set to 0 (default) no checking of the time is done. Change default value of this parameter only if there is a clear reason to do so.

Maximum number of iterations:
The limit for the number of iteration (fitting stops earlier if all convergence criteria are satisfied).

Number of iterations per fitting step:
Indicates how many iterations are carried out before a signal to break from the user can be processed and the data on the screen is updated.

Extended parameter setup allows to change default settings of individual convergence criteria for fitted parameters. A convergence criterion is satisfied when the change in the parameter value does not exceed the predefined level. Convergence criteria may be absolute or relative (type of the criterion is indicated by the buttons visible in the extended setup). Selecting No button for any parameter disables its convergence criterion (numerical value of previous setting remains visible).

Simulation control parameters

Most of the simulation options are set automatically by the program. In the choice of their values the program assumes that the parameters of the electrode process have moderate values and tries to find a reasonable compromise between results precision and the calculation time. However, when extreme values of parameters (or extreme combinations of values) are set, or when very high accuracy is desired, automatic settings may be insufficient.
The simulation options are set by choosing Fit control parameters from the Option menu. The middle part of the appearing window contains parameters that control the way the calculations are carried out. These parameters are presented below:

Minimal number of simulation steps per potential value:
The minimal number of simulations cycles carried out for each value of the potential. If this value is set to *N*, then each potential step time is divided into *N* subintervals and the simulation is carried out for each of these subintervals with time step equal to 1/*N* fraction of the step time. The default value is 4.

Maximal number of simulation steps per potential value:
The upper limit for the previous parameter.

Number of points in concentration gradient calculation:
The value of the current is calculated from the derivative of the reactant concentration at the electrode surface. In digital simulation, the values of concentrations are discrete and defined only in grid points, and in calculations of concentration gradient the specified number of points is used. Use of many points usually gives a better precision of the calculated current. On the other hand, the increase of number of the datapoints significantly increases the execution time. The default value for this parameter is 2.

Parameter A in space transformation y=ln(1+Ax):
To speed up the calculations, the space grid exponentially expands with the distance from the electrode surface. This is obtained by transforming the space in such a way, that the increasing distances in the real space correspond to equally spaced distances in the transformed space. The program uses Feldberg's function y=ln(1+*A*x) for space transformation and the rate of expansion, thus also the number of points in concentration profile, is controlled by parameter *A*. This parameter should be in the range 2...3, and its default setting is 2.

Use LU decomposition for boundary condition:
This is the option to provide an alternative way to solve the matrix representing boundary condition at the electrode surface. The matrix is highly sparse and it is usually solved by direct method. However, it can happen that the LU (=Lower/Upper) decomposition method gives better results in some cases, but it is significantly slower when the number of points used to calculate concentration gradient increases. Default setting is not to use LU method.

Fast Fit parameters

See "Fitting in more detail, Full and Fast fit".

Data reduction factor:
Allows to carry out fast fit with a data set reduced by this factor (in the reduced data set points are evenly spaced). The actual value of this factor depends also on the minimal number of points for fast fit (For more information consult "Fitting: Fast and Full fit").

Minimum number of points for Fast Fit:
This is the limit for the data reduction factor. The data set used for fast fitting cannot have fewer points than set by this parameter.

Maximum number of iterations for Fast Fit:
The limit for the iteration number. After reaching it, the fitting procedure switches to regular fit with all data points.

Fitting in more detail

Fast and Full fit

When working with larger data sets (over 200 points), often obtained in cyclic voltammetry, it may be attractive to speed up fitting by getting raw values of parameters with a reduced data set and then to refine them using full set. For this purpose one can use the reduced data set fitting feature of the fit and simulation program.
In the reduced data set only every *N*-th point is used in the fitting. The number *N* is called Data reduction factor. Certainly, this factor cannot be very high because fitting with very few points is likely to deliver parameter values that are not much better than the initial guesses the program can make. Therefore the user can define the minimal number of points that the reduced data set must contain. The actual reduction factor is the smaller number from the data reduction value set and the (total datapoints)/(minimal datapoints) ratio. Data reduction factor equal to 1 means that no Fast Fit is performed.
Parameters to control Fast Fit can be set in a window activated by option “Fit control parameters” from Option menu. In the lower part of this window the data reduction factor, minimal number of points in the reduced data set and the maximal number of Fast Fit iterations can be set. Using Fast Fit can be particularly useful when initial guesses do not deliver good estimates of the parameters, or when fitting process tends to oscillate.

Choosing parameters to fit

Each model is defined by a number of parameters. These parameters are measurement parameters (e.g., start potential, scan rate), general parameters (e.g., temperature) and specific parameters (e.g., diffusion coefficient, standard redox potential etc.).
From these parameters only some can be fitted and they are called fitable parameters. The general rule is that only specific parameters can be fitted. From them, parameters that can acquire only certain values (for example: the number of electrons involved in the process) are not fitable.
It is only possible to fit successfully parameters that are independent on each other, i.e., change in the model due to variation of a certain parameter cannot be obtained by combination of variations of other parameters. Although models are built in such a way that interdependent parameters are avoided, it can happen that the particular data set renders two parameters dependent or partially dependent. An example of such situation is a data set obtained in cyclic voltammetry with a quasi-reversible system: if scan potentials are chosen so that only one peak (cathodic or anodic) is visible, it is impossible to determine both the heterogeneous reaction rate k_s and the formal potential E^o of the redox couple.
How to detect dependence of parameters is explained in "Finding interdependence of fitted parameters".

Initial guesses

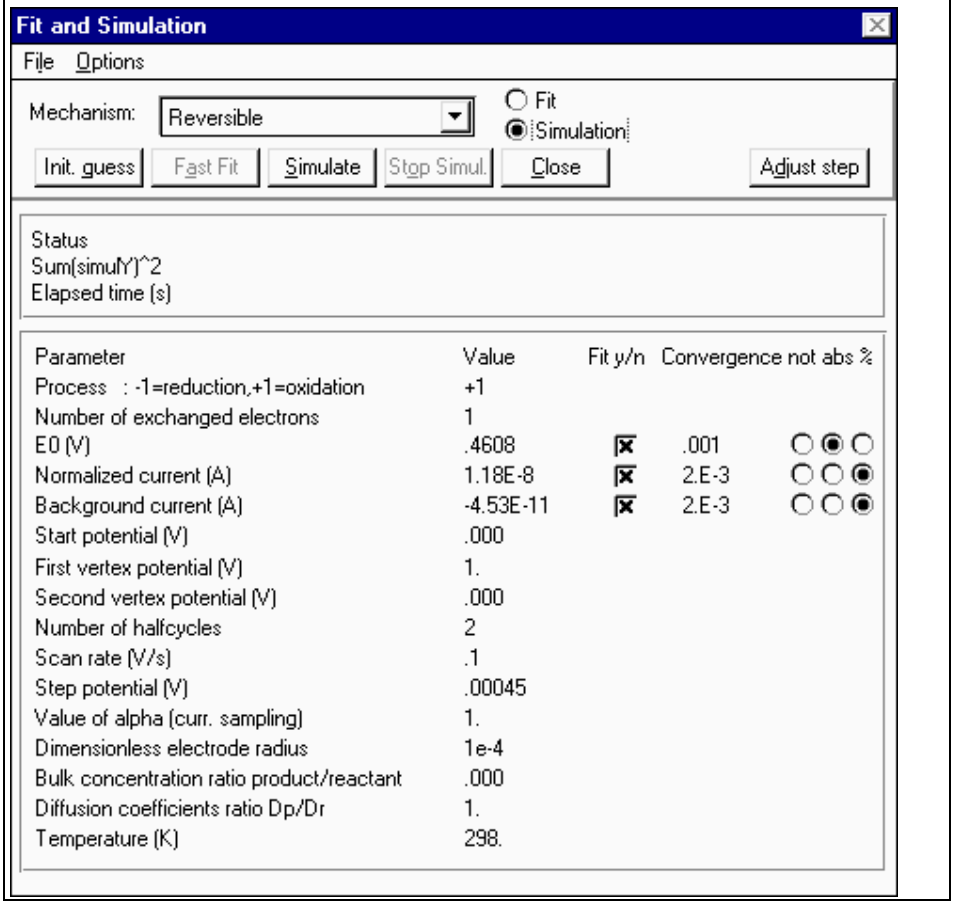
The program provides initial guesses for most of the fitable parameters. The exact list of parameters for which initial guesses are calculated is available in the description of the models.
To calculate initial guesses of the parameters, click the button Init. guess, select option “Initial guesses” from the Option menu or press Alt-I. Initial guesses will appear on the screen. Also the type of the process (reduction or oxidation) is set to the default value: reduction for scans going toward negative potentials, and oxidation for scans going toward positive potentials. The type of the process is an extended setup parameter, that can be inspected and modified when extended parameter mode is on (Ctrl-E or the Extended setup option from the Options menu).
To check the correctness of initial guesses before starting the actual fit, switch the mode to simulation (option button near the model name) and then click the Simulate button. A curve will be simulated with the current parameter settings, and displayed in Data Presentation window. If initial guesses are satisfactory, switch back to fit mode and proceed with fitting. Special care in checking is required for the number of Exchanged electrons and the Dimensionless electrode radius.

Adjust step size

The fit and simulation option for CV automatically searches for the potential step in the CV-data. However the data can sometimes have an non-equidistant step in the potential data (i.e. if measured with ADC750). The fit and simulation software assumes an equidistant step in the potential. Therefor the fit can give error messages. In order to get rid of these error messages, an option to adjust the step to the step potential from the procedure is available. The button is visible on the Fit and simulation window when the ‘Extended setup’ is activated. Please note that the kinetic parameters, as a result of this fit, are not reliable anymore.

Convergence criteria

Fig. 52 *Convergence criteria*



Fitting process is carried out until convergence criteria are satisfied or either the iteration limit or time limit is reached. There are two types of convergence criteria: based on χ^2 and related to the parameter value change.

Criteria based on χ^2 demand that:

1. change of χ^2 in the last iteration step must be negative (χ^2 decreases)
2. value of χ^2 (weighted with σ_0) should be less than 1 (or less than $\sum_i y_i^2$ for unweighted data)
3. the last change in χ^2 is so small, that it can be neglected. The value that can be neglected is defined by the user as the maximal relative in χ^2 (Option menu, "Fit control parameters"). The default maximal change is 0.01 (=1%) of χ^2 value.

Criteria related to fitted parameters value require, that the change to the parameter value in the last iteration should not exceed a certain value. This value can be defined as an absolute, or as a relative one (a fraction of the parameter's value). In the extended setup (Option menu) it is possible to define the value and the type (absolute/relative) of the convergence criterion for each fitable parameters. The

Convergence field contains the criterial value, and the buttons right to the value field can be used to select the absolute type of the criterion, the relative one or to disable the criterion for this parameter. The fitting process finishes when all the convergence criteria are satisfied. If the convergence is not reached in spite of many interactions done, this can be due to the following reasons:

1. Demanded precision of the parameters is unrealistic. The level of noise in the data, or precision of the measured variable (usually current) may keep the variation of the parameter of interest above the demanded level.
2. The type of the criterion is not appropriate. For example, in datasets where the background is very small it is better to use the absolute criterion than the relative one for background value, and relate it to the measured peak or wave current.

The model is not applicable. In this situation the value of χ^2 is usually larger than 1 (or larger than $\sum_i y_i^2$ for unweighted data) while all other criteria can be met. It is then advisable to either change the model, of re-examine settings for non-fitable parameters, like the number of electrons involved in the electrode reaction.

Finding interdependence of fitted parameters

Dependence of parameters can be detected by inspection of the covariance matrix (Covariance matrix in the Option menu or Ctrl-M). The diagonal terms are unity. If a term corresponding to a pair of parameters is significant, there is a serious chance that these two parameters are interdependent.
Problems can arise if two or more parameters are interdependent. The matrices used during fit can become singular and an error occurs. Also, the fitted values of interdependent parameters are meaningless, or the program oscillates and it cannot deliver the final values. Finally, the computational time unnecessary increases, because fitting of each parameter requires the calculation of the derivative of the fitted curve with respect to this parameter. Some derivatives can be calculated analytically, but some not, and in the latter case the derivative must be obtained numerically. This requires an additional simulation per iteration step.

Fit and simulation error messages

error -1: "xxxxxxx":
Internal error of the fit and simulation program. String "xxxxxxx" contains specific information about the problem. Please report circumstances under which this error appeared.

error 1: Not enough memory:
There is not enough memory available to carry out the simulation. Try to free some memory by closing other applications.

error 10: Technique not supported:
An operation has been requested that is not supported for the currently selected technique. Please report circumstances under which this error appeared.

error 11: Mechanism not supported:
An operation has been requested that is not supported for this electrode reaction mechanism. Please report circumstances under which this error appeared.

error 12: Model not supported:
An operation has been requested that is not supported for the model chosen. Please report circumstances under which this error appeared.

error 20: Negative reactant concentration obtained:
Negative concentration of the reactant at the electrode surface has been obtained during the simulation of concentration profiles. This is usually due to the extreme value of the potential, at which the ratio of reactant to product concentration is either very small or very large. The general remedy is to shorten the potential range used. If it is not possible, try to use another settings for advanced simulation parameters. If this doesn't help, please report the problem.

error 21: Negative product concentration obtained:
Negative concentration of the product at the electrode surface has been obtained during the simulation of concentration profiles. This is usually due to the extreme value of the potential, at which the ratio of reactant to product concentration is either very small or very large. The general remedy is to shorten the potential range used. If it is not possible, try to use another settings for advanced simulation parameters. If this doesn't help, please report the problem.

error 51: GAUSSJ: Singular Matrix-1:
Two or more parameters in the model are dependent or nearly dependent.

error 52: GAUSSJ: Singular Matrix-2:
Two or more parameters in the model are dependent or nearly dependent.

Descriptions of the models

General remarks

All models of electrode reactions assume diffusion to an electrode with finite dimensions. The size of the electrode is characterised by the dimensionless electrode radius

$$r_d = r_e / \sqrt{D_R \tau}$$

where r_e is the radius in meters, D_R is the diffusion coefficient of the reactant in m^2/s and τ is the characteristic time parameter of the technique. The time parameter τ is equal to RT/nFV (in staircase and cyclic voltammetry, V=scan rate), to pulse time (in normal pulse voltammetry and chrono techniques), to modulation time (in differential pulse techniques) and to inverse of frequency (in square wave voltammetry).
If the electrode is large or the τ parameter is small (fast experiments), i.e., only linear diffusion takes place, the dimensionless electrode radius should be set to zero. This value indicates that the radius of the electrode is irrelevant. All electron transfer rates are normalised according to equation

$$\bar{k} = k\sqrt{\tau / D_R}$$

and all homogeneous (chemical) reaction rates are normalised by multiplication by τ

$\bar{k}_{chem} = k_{chem}\tau$

Use of normalised constants allows carrying out fitting without the knowledge of diffusion coefficients.

In all equations in the description of the models the log() function refers to 10-based logarithm, and ln() function to natural (*e*-based) logarithm.

Cyclic voltammetry: reversible electrode process

Reaction equation: $R \xleftrightarrow{ne^-} P$
Fitable parameters:
redox potential E^0 (V)
normalised current I_{norm} ($I = I_{norm}*\chi(at)$) (A)
constant background current (A)
Initial guesses available for: number of exchanged electrons, E^0, I_{norm}, background current
Comments: According to the theory, the peak current is equal to $nFAc_{bulk}(\pi aD)^{1/2}*\chi(at)$, where the first term is equal to the fitable parameter I_{norm} and the function $\chi(at)$, $a=nFV/RT$, V being scan rate, represents the shape of the voltammetric peak. The peak value of this function is 0.4463 for linear sweep voltammetry, while for voltammetry utilising the staircase voltage ramp the exact value depends on the step height, step time and the current sampling parameter α. Details regarding the function $\chi(at)$ can be found in literature[1].

Cyclic voltammetry: quasi-reversible electrode process

Reaction equation: $R \xleftrightarrow{ne^-,k_s} P$
Fitable parameters:
redox potential E^0 (V)
Log (normalised electron transfer rate), $\log(\bar{k}_s)$
transfer coefficient α
normalised current I_{norm} ($I = I_{norm}*\chi(bt)$) (A)
constant background current (A)
Initial guesses available for: number of exchanged electrons, $\log(k_s)$, E^0, I_{norm}, background current
Comments: The parameter $\log(\bar{k}_s)$ is a 10-base logarithm of the electron transfer rate, normalised with respect to the time scale of the experiment $\bar{k}_s = k_s\sqrt{RT/nFVD}$, where V is the scan rate and k_s is the electron transfer rate used in Butler-Volmer equation

[1] R. S. Nicholson and I. Shain, Anal. Chem., vol. 36, 1964, page 706.

$$I = k_s\left(c_R \exp\left(-\alpha nF/RT\left(E - E^0\right)\right) + c_P \exp\left((1-\alpha nF)/RT\left(E - E^0\right)\right)\right)$$

According to the theory, the peak current is equal to $nFAc_{\text{bulk}}(\pi bD)^{1/2}{*}\chi(bt)$, where the first term is equal to the fitable parameter I_{norm} and the function $\chi(bt)$, $b=\alpha nFV/RT$, represents the shape of the voltammetric peak. The peak value of this function depends on the electron transfer rate k_s, the transfer coefficient α, the step height, step time and the current sampling parameter α.

Cyclic voltammetry: irreversible electrode process

Reaction equation: $R \xrightarrow{ne^-,k_s} P$
Fitable parameters:

Log(Normalised electron transfer rate at E^0=0), $\log\left(\bar{k}^0_{fh}\right)$
(exchanged electrons)*(transfer coefficient) αn
normalised current I_{norm} ($I = I_{\text{norm}}{*}\chi(bt)$) (A)
constant background current (A)

Initial guesses available for: E^0, αn, I_{norm}, background current
Comments: The parameter $\log\left(\bar{k}^0_{fh}\right)$ is a 10-base logarithm of the electron transfer rate, normalised with respect to the time scale of the experiment $\bar{k}^0_{fh} = k^0_{fh}\sqrt{RT/nFVD}$, where V is the scan rate and k^0_{fh} is the electron transfer rate at E=0, used in reduced Butler-Volmer equation

$$I = k^0_{fh} c_R \exp\left(\left(-\alpha nF/RT\right)E\right) = k_s c_R \exp\left(\left(-\alpha nF/RT\right)\left(E - E^0\right)\right)$$

According to the theory, the peak current is equal to $nFAc_{\text{bulk}}(\pi bD)^{1/2}{*}\chi(bt)$, where the first term is equal to the fitable parameter I_{norm} and the function $\chi(bt)$, $b=\alpha nFV/RT$, represents the shape of the voltammetric peak. The peak value of this function is equal to 0.4958 for linear sweep voltammetry, and for staircase voltammetry it depends on the electron transfer rate k_s, the transfer coefficient α, the step height, step time and the current sampling parameter α. Details regarding the function $\chi(bt)$ can be found in literature.
There is no need to set the number of exchanged electrons, because the term αn is fitted as a whole.

Cyclic voltammetry: reversible electrode process followed by irreversible chemical reaction (ECi)

Reaction equation: $R \xleftrightarrow{ne^-} P \xrightarrow{k_{cf}} B$
Fitable parameters:

redox potential E^0 (V)
forward chemical reaction rate kc(foll)-> (norm.) = k_{cf}
normalised current I_{norm} ($I = I_{\text{norm}}{*}\chi(bt)$) (A)
constant background current (A)

Initial guesses available for: number of exchanged electrons, E^0, I_{norm}, background current

Comments: The forward chemical reaction rate is normalised with respect to the time scale of the voltammetric experiment, $\bar{k}_{cf} = k_{cf}\left(RT/nFV\right)$. Similarly to previous cases, the voltammetric peak current is expressed as a product of the peak shape function $\chi(bt)$ and the term including the electrode area, concentration, diffusion coefficient and the number of exchanged electrons. Details regarding this mechanism can be found in literature.

Cyclic voltammetry: two-component models

Two-component models represent the situation when two electroactive species are reduced or oxidised at the electrode independently from each other. In such situations their peaks can overlap, what hinders the extraction of relevant parameters for separate reactions.

There is a number of two-component models available, differing in the degree of reversibility of each electron transfer (reversible, quasi-reversible or irreversible mechanism). The parameters are denoted with numbers 1 and 2 to indicate to which component they correspond.

Reaction equations for single component:

$R_i \xleftrightarrow{ne^-} P_i$ (reversible process)

$R_i \xleftrightarrow{ne^-,k_s} P_i$ (quasi-reversible process)

$R_i \xrightarrow{ne^-,k_s} P_i$ (irreversible process)

Fitable parameters

- *reversible case:*
  - redox potential E^0 (V)
  - normalised current I_{norm} ($I = I_{norm}*\chi(at)$) (A)
- *quasi-reversible case:*
  - redox potential E^0 (V)
  - Log(normalised electron transfer rate), $\log\left(\bar{k}_s\right)$)
  - transfer coefficient α
  - normalised current I_{norm} ($I = I_{norm}*\chi(bt)$) (A)
- *irreversible case:*
  - Log(Normalised electron transfer rate at E^0=0), $\log\left(\bar{k}^0_{fh}\right)$
  - (exchanged electrons)*(transfer coefficient) αn
  - normalised current I_{norm} ($I = I_{norm}*\chi(bt)$) (A)
- *common parameter:*
  - constant background current (A)

Initial guesses available for:

Comments: According to the theory, the peak current is equal to $nFAc_{bulk}(\pi aD)^{1/2}*\chi(at)$ (reversible processes) or $nFAc_{bulk}(\pi bD)^{1/2}*\chi(bt)$ (irreversible processes), where the first term is equal to the fitable parameter I_{norm} and the functions $\chi(at)$ and $\chi(bt)$ represent the shape of the voltammetric peak. The parameters *a* and *b* are respectively $a=nFV/RT$, $b=\alpha nFV/RT$, *V* being the scan rate. The peak values of these function are 0.4463 (reversible) and 0.4958 (irreversible) for linear sweep voltammetry. If voltammetry with staircase voltage ramp is used, the exact value

depends on the step height, step time and the current sampling parameter α. Details regarding the function $\chi(at)$ and $\chi(bt)$can be found in literature.
The electron transfer rates $\bar{k}_s$ and $\bar{k}^0_{fh}$ are defined as follows:
$\bar{k}^0_{fh} = k^0_{fh}\sqrt{RT/nFVD}$ and $\bar{k}_s = k_s\sqrt{RT/nFVD}$
while the Butler-Volmer equations for respectively quasi-reversible and irreversible processes are
$I = k_s\left(c_R \exp\left(-\alpha nF/RT\left(E - E^0\right)\right) + c_P \exp\left((1-\alpha nF)/RT\left(E - E^0\right)\right)\right)$ (quasi-reversible)
$I = k^0_{fh} c_R \exp\left(\left(-\alpha nF/RT\right)E\right) = k_s c_R \exp\left(\left(-\alpha nF/RT\right)\left(E - E^0\right)\right)$ (irreversible)
Due to the possible complication of two-component voltammograms, it can happen that the initial guesses are inferior to those obtained in simpler models. However, it is always possible to select datapoints (by setting the window in such a way that only one peak is covered), do initial guesses for one-component model and transfer the results to two-component model.
When electron transfer processes are different, for example Er+Ei, all parameters marked with (1) refer to electron transfer Er, while all marked with (2) - to electron transfer Ei. The initial guess procedure can have problems with appropriate assignment of peaks to the components. This assignment can be changed by swapping the values referring to the first component and to the second component. In case of irreversible electron transfer it is necessary, however, to adjust the value of $\bar{k}^0_{fh}$ using the relationship $\Delta k^0_{fh} = \alpha nF\Delta E_p/RT \log e$.

Normal pulse voltammetry: reversible electrode process

Reaction equation: $R \xleftrightarrow{ne^-} P$
Fitable parameters:
halfwave potential $E_{1/2}$ (V)
limiting current I_{lim} (A)
constant background current (A)
Initial guesses available for: number of exchanged electrons, $E_{1/2}$, I_{lim}, background current
Comments: The theoretical expression for the limiting current at a large flat electrode is $I_{\text{lim}}=nFAc_{\text{bulk}}(D_R/\pi t_p)^{1/2}$, where t_p is the pulse time. The halfwave potential should be equal to polarographic halfwave potential.

Normal pulse voltammetry: quasi-reversible electrode process

Reaction equation: $R \xleftrightarrow{ne^-,k_s} P$
Fitable parameters:
redox potential E^0 (V)
Log(normalised electron transfer rate), $\log\left(\bar{k}_s\right)$
transfer coefficient α
limiting current I_{lim} (A)
constant background current (A)

Initial guesses available for: number of exchanged electrons, E^0, I_{norm}, background current

Comments: The parameter $\log(\bar{k}_s)$ is a 10-base logarithm of the electron transfer rate, normalised with respect to the time scale of the experiment $\bar{k}_s = k_s\sqrt{t_p/D}$, where t_p is the pulse time and k_s is the electron transfer rate used in Butler-Volmer equation

$$I = k_s\left(c_R \exp\left(-\alpha nF/RT\left(E - E^0\right)\right) + c_P \exp\left((1-\alpha nF)/RT\left(E - E^0\right)\right)\right)$$

The theoretical expression for the limiting current at a large flat electrode is $I_{lim}=nFAc_{bulk}(D/\pi t_p)^{1/2}$.

Normal pulse voltammetry: irreversible electrode process

Reaction equation: $R \xrightarrow{ne^-, k_s} P$

Fitable parameters:

Characteristic potential E^* (V)

Log(Normalised electron transfer rate at E^0=0), $\log\left(\bar{k}^0_{fh}\right)$

(exchanged electrons)*(transfer coefficient) αn

limiting current I_{lim} (A)

constant background current (A)

Initial guesses available for: $\log\left(\bar{k}^0_{fh}\right)$, αn, E^*, I_{norm}, background current

Comments: There is no need to set the number of exchanged electrons, because the term αn is fitted as a whole. The theoretical expression for the limiting current at a large flat electrode is $I_{lim}=nFAc_{bulk}(D/\pi t_p)^{1/2}$, where t_p is the pulse time. The characteristic potential E^* is defined as $E^* = \left(RT/\alpha nF\right)\ln\bar{k}^0_{fh} = E^0 + \left(RT/\alpha nF\right)\ln\bar{k}_s$, where $\bar{k}^0_{fh} = k^0_{fh}\sqrt{t_p/D}$ and $\bar{k}_s = k_s\sqrt{t_p/D}$. k_s and k^0_{fh} are the electron transfer rates used in Butler-Volmer equation

$$I = k^0_{fh}c_R \exp\left(\left(-\alpha nF/RT\right)E\right) = k_s c_R \exp\left(\left(-\alpha nF/RT\right)\left(E - E^0\right)\right)$$

Normal pulse voltammetry: reversible electrode process followed by irreversible chemical reaction (ECi)

Reaction equation: $R \xleftrightarrow{ne^-} P \xrightarrow{k_{cf}} B$

Fitable parameters:

redox potential E^0 (V)

forward chemical reaction rate kc(foll)-> (norm.) $\bar{k}_{cf}$

limiting current I_{lim} (A)

constant background current (A)

Initial guesses available for: number of exchanged electrons, E^0, I_{norm}, background current

Comments: The theoretical expression for the limiting current at a large flat electrode is $I_{lim}=nFAc_{bulk}(D/\pi t_p)^{1/2}$, where t_p is the pulse time. The forward chemical reaction rate is normalised with respect to the time scale of the experiment, $\bar{k}_{cf} = k_{cf} t_P$.

Normal pulse voltammetry: reversible electrode process (analytical), quasi-reversible electrode process (analytical) and irreversible electrode process (analytical)

These models differ from the previous only by the fact, that each point of the normal pulse voltammogram is calculated from analytical expressions for chronoamperometry under the following assumptions:

- the current is measured at the end of the potential pulse
- before each potential pulse concentrations of the species at the electrode surface are the same as in the bulk of the solution

The latter means that no significant electrode reaction occurs at the base potential, and that the interval time is long enough to restore the initial concentrations (or the dropping mercury electrode is used). In addition to this, it is assumed in the reversible model that the product of the electrode reaction is initially absent in the solution. Thanks to analytical expressions the speed of calculations is much higher than in the regular model based on finite-difference simulation. Therefore, if the mentioned assumptions are valid, this model should be preferred.

Differential pulse voltammetry: reversible electrode process

Reaction equation: $R \xleftrightarrow{ne^-} P$
Fitable parameters:
peak potential E_p (V)
peak current I_p (A)
constant background current (A)
Initial guesses available for: number of exchanged electrons, E_p, I_p, background current
Comments: The approximate expression for the peak height, valid under linear diffusion conditions, is

$$I_p = nFAc_{bulk}(D/\pi t_m)\tanh(nF\Delta E/4RT)$$

where t_m is the modulation time and ΔE is the modulation amplitude.

Differential pulse voltammetry: quasi-reversible electrode process

Reaction equation: $R \xleftrightarrow{ne^-,k_s} P$
Fitable parameters:
peak potential E_p (V)
Log(normalised electron transfer rate), $\log(\bar{k}_s)$
transfer coefficient α
peak current I_p (A)
constant background current (A)

Initial guesses available for: number of exchanged electrons, E_p, $\log(\bar{k}_s)$, α, I_p, background current

Comments: The parameter $\log(\bar{k}_s)$ is a 10-base logarithm of the electron transfer rate, normalised with respect to the time scale of the experiment, $\bar{k}_s = k_s\sqrt{t_m/D_R}$, where V is the scan rate and k_s is the electron transfer rate used in Butler-Volmer equation

$$I = k_s\left(c_R \exp\left(-\alpha nF/RT\left(E-E^0\right)\right)+c_P \exp\left((1-\alpha)nF/RT\left(E-E^0\right)\right)\right)$$

The general expression for the peak height does not exist, expressions for particular situations are complicated.

Differential pulse voltammetry: irreversible electrode process

Reaction equation: $R \xrightarrow{ne^-,k_s} P$

Fitable parameters:

Characteristic potential E^* (V)

Log(Normalised electron transfer rate at E^0=0), $\log(\bar{k}^0_{fh})$

(exchanged electrons)*(transfer coefficient) αn

peak current I_p (A)

constant background current (A)

Initial guesses available for: number of exchanged electrons, E_p, $\log(\bar{k}^0_{fh})$, αn, I_p, background current

Comments:

There is no need to set the number of exchanged electrons, because the term αn is fitted as a whole.

The characteristic potential E^* is defined as $E^* = (RT/\alpha nF)\ln\bar{k}^0_{fh} = E^0 + (RT/\alpha nF)\ln\bar{k}_s$, where $\bar{k}^0_{fh} = k^0_{fh}\sqrt{t_m/D_R}$ and $\bar{k}_s = k_s\sqrt{t_m/D_R}$. k_s and k^0_{fh} are the electron transfer rates used in Butler-Volmer equation

$$I = k^0_{fh}c_R \exp\left(\left(-\alpha nF/RT\right)E\right) = k_s c_R \exp\left(\left(-\alpha nF/RT\right)\left(E-E^0\right)\right)$$

Differential pulse voltammetry: reversible electrode process followed by irreversible chemical reaction (ECi)

Reaction equation: $R \xleftrightarrow{ne^-} P \xrightarrow{k_{cf}} B$

Fitable parameters:

redox potential E^0 (V)

normalised forward chemical reaction rate kc(foll)-> (norm.), $\bar{k}_{cf}$

peak current I_p (A)

constant background current (A)

Initial guesses available for: E_p, I_p, background current

Comments: The forward chemical reaction rate is normalised with respect to the time scale of the voltammetric experiment, $\bar{k}_{cf} = k_{cf} t_m$. No simple expression is available for the peak height.

Square wave voltammetry: reversible electrode process

Reaction equation: $R \xleftrightarrow{ne^-} P$
Fitable parameters:
formal potential E^0 (V)
peak current I_p (A)
constant background current (A)
Initial guesses available for: E_p, I_p, background current (fitting on net current)
E_{pf}, I_{pf}, background current (fitting on forward/backward current)
Comments: There is no simple expression for the net peak current. The interpretation of the value of I_p depends whether fitting takes place on the net current or on forward/backward currents: in the first case Ip corresponds to the height of the net current, in the second - to the height of the forward peak. Switching between net current and forward/backward current will therefore result in the difference in peak heights.
The potential of the peak is very close to the polarographic halfwave potential.

Square wave voltammetry: quasi-reversible electrode process

Reaction equation: $R \xleftrightarrow{ne^-,k_s} P$
Fitable parameters:
formal potential E^0 (V)
Log(normalised electron transfer rate), $\log(\bar{k}_s)$
transfer coefficient α
peak current I_p (A)
constant background current (A)
Initial guesses available for: E_p, I_p, background current
Comments: The parameter $\log(\bar{k}_s)$ is a 10-base logarithm of the electron transfer rate, normalised with respect to the time scale of the experiment $\bar{k}_s = k_s / \sqrt{fD_R}$, where f is the frequency and k_s is the electron transfer rate used in Butler-Volmer equation

$$I = k_s \left(c_R \exp\left(-\alpha nF/RT\left(E - E^0\right)\right) + c_P \exp\left((1-\alpha)nF/RT\left(E - E^0\right)\right)\right)$$

There is no simple expression for the net peak current. The interpretation of the value of I_p depends whether fitting takes place on the net current or on forward/backward currents: in the first case Ip corresponds to the height of the net current, in the second - to the height of the forward peak. Switching between net current and forward/backward current will therefore result in the difference in peak heights.

Square wave voltammetry: irreversible electrode process

Reaction equation: $R \xrightarrow{ne^-,k_s} P$
Fitable parameters:

Characteristic potential E^* (V)

Log(normalised electron transfer rate at E0=0), $\log\left(\bar{k}^0_{fh}\right)$

(exchanged electrons)*(transfer coefficient) αn

peak current I_p (A)

constant background current (A)

Initial guesses available for: E^*,I_p, background current

Comments: There is no need to set the number of exchanged electrons, because the term αn is fitted as a whole.

The characteristic potential E^* is defined as

$E^* = \left(RT/\alpha nF\right)\ln \bar{k}^0_{fh} = E^0 + \left(RT/\alpha nF\right)\ln \bar{k}_s$, where $\bar{k}^0_{fh} = k^0_{fh} \big/ \left(fD_R\right)$ and

$\bar{k}_s = k_s \big/ \left(fD_R\right)$ $\bar{k}_s = k_s\sqrt{\left(RT/nFV\right)/D}$. where f is the frequency and k_s and k^0_{fh} are the electron transfer rates used in simplified Butler-Volmer equation

$$I = k^0_{fh} c_R \exp\left(\left(-\alpha nF/RT\right)E\right) = k_s c_R \exp\left(\left(-\alpha nF/RT\right)\left(E - E^0\right)\right)$$

There is no simple expression for the net peak current. The interpretation of the value of I_p depends whether fitting takes place on the net current or on forward/backward currents: in the first case Ip corresponds to the height of the net current, in the second - to the height of the forward peak. Switching between net current and forward/backward current will therefore result in the difference in peak heights.

Square wave voltammetry: reversible electrode process followed by irreversible chemical reaction (ECi)

Reaction equation: $R \xleftrightarrow{ne^-} P \xrightarrow{k_{cf}} B$

Fitable parameters:

redox potential E^0 (V)

normalised forward chemical reaction rate kc(foll)-> (norm.) $\bar{k}_{cf}$

peak current I_p (A)

constant background current (A)

Initial guesses available for: E_p, I_p, background current

Comments: The forward chemical reaction rate is normalised with respect to the time scale of the experiment, $\bar{k}_{cf} = k_{cf} / f$, where f is the frequency.

There is no simple expression for the net peak current. The interpretation of the value of I_p depends whether fitting takes place on the net current or on forward/backward currents: in the first case Ip corresponds to the height of the net current, in the second - to the height of the forward peak. Switching between net current and forward/backward current will therefore result in the difference in peak heights.

4.14 Current density

The current density is calculated with the surface area, using the surface area on page 2 of the procedure window.

4.15 WE2 versus WE plot

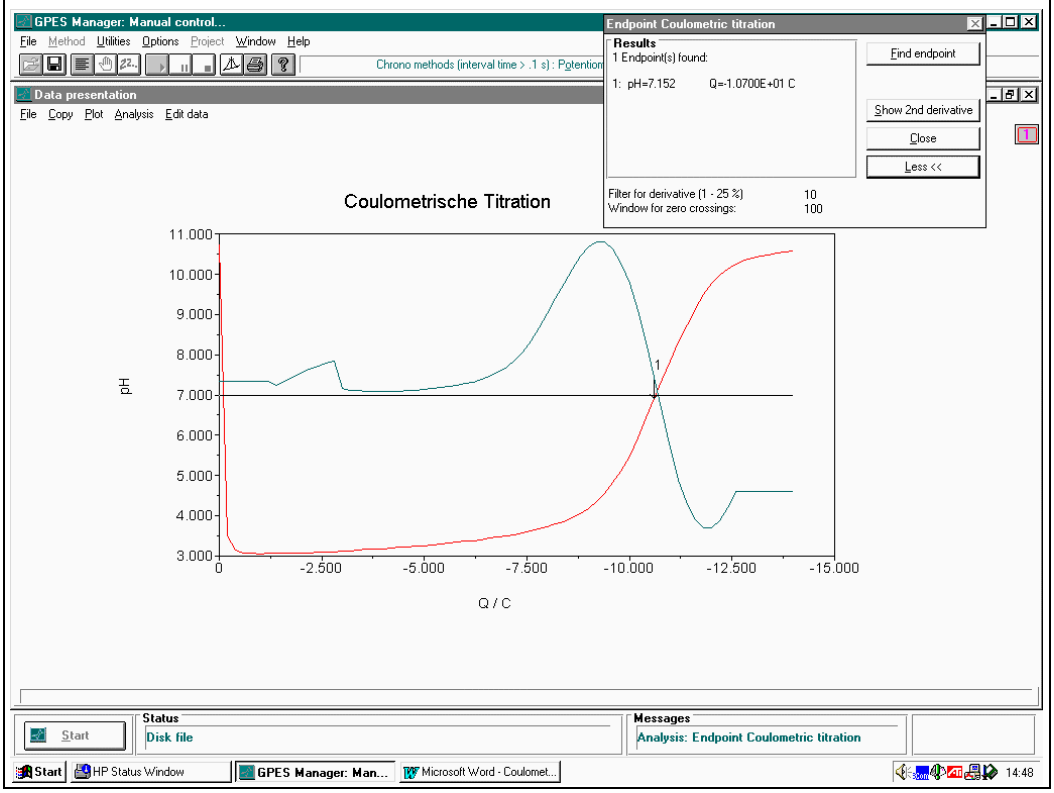
When a BIPOT is present, Iring versus Idisk plots can be constructed with this option.

4.16 Endpoint Coulometric titration

After performing a coulometric titration experiment (Chrono method (>0.1s) potentiometry (galvanostatic) with pX/pH signal) this option can be chosen.
The experiment time is converted into charge (the current applied is given from the procedure) and only the pX/pH signal is shown on the y-axes. Furthermore the 'Endpoint Coulometric titration' window is opened, to find the endpoint. If you follow the instructions the turning point will be shown as endpoint.

- The endpoint is obtained from the zero crossing(s) in the 2^{nd} derivative. The 2^{nd} derivative and endpoint are calculated using the last applied level. If only one level is defined all calculations are done on this particular level.
- The 2^{nd} derivative values are normalised so do not pay attention to the absolute values. The 2^{nd} derivative plot is used for indicative purposes only.
- The show 2^{nd} derivative button is active after the Find endpoint button has been pressed.
- The 'Show last level' button appears only if more then one level is measured.
- If the amount of measured point is poor the indicated end point in the curve can be slightly different from the actual zero crossing in the 2^{nd} derivative. The pointer can only be set on a real data-point and not on an interpolated point in between.

Fig 52a. *Coulometric titration plot*



Parameters:

Filter for derivative:	Filter factor to reduce noise on the 2nd derivative. 1%: no filtering – 25%: heavy filtering.
Window for zero crossings:	Defines when a zero crossing should be noticed as a real zero crossing. This window defines the amount of points with different sign before and after the zero crossing.

Due to Faraday's law the equivalent of generated titrant is proportional to the charge and the equivalent of the analyte can be calculated (see also Application note "Coulometric titration", and "Installation and Diagnostics Guide: pX-module).

5. Editing of measured data

5.1 Smooth

Every measurement is disturbed by noise. In many cases the noise level will be low, but especially at low current levels the amount of noise can be severe. In order to enhance the signal to noise ratio of experimental data sets, a Smooth option is supplied. The data files can be smoothed using either the Savitsky-Golay algorithm or a FFT-algorithm.

Smoothing can be performed on the whole curve or a part of it. When only a part of the curve should be smoothed, click the Smooth window button and select a part of the curve. The remainder will not be smoothed. This option is only available for Savitzky and Golay smoothing.

The popular Savitzky and Golay method is described in Anal. Chem.,36,1627 (1964). Their method presumes that a number of points can be fitted to a polynomial so that the best curve will pass through the experimental points. This method is also called weighted moving averaging. Before the smooth routine of Savitzky and Golay is applied to the data set, spikes in the set of data are removed.
The Smooth option in all programs first asks which smooth level has to be applied. Valid levels are 0 to 4.

These levels are :
0- spike rejection only
1- spike rejection and a 5-point weighed moving average
2- spike rejection and a 9-point weighed moving average
3- spike rejection and a 15-point weighed moving average
4- spike rejection and a 23-point weighed moving average

The applicable smooth level heavily depends on the number of points of the data set. The more points within the curve, the higher the smooth level can be without modifying the curve too much.

Having selected the FFT option, a logarithmic or linear frequency domain plot is displayed. Now a cutoff frequency has to be supplied, which should be less than the dominant noise frequency. The FFT-smoothing algorithm assumes that the signal is composed of n/2 sine waves of different frequencies, where n is the number of measured data points, filled up to a power of 2 (512, 1024, etc.). The added data points get a value of zero. A cut-off frequency of for instance 20 means that the amplitudes of the 20 sine waves with the lowest frequencies are kept, all other amplitudes are set to zero. After a back-transformation, both the original curve and the smoothed curve are displayed and the question is posed whether the original data should be replaced. The FFT-algorithm is very effective in removing noise originating from the power-source. The FFT-algorithm is explained in the book "Numerical Recipes", W.H. Press et al., Cambridge University Press, ISBN 0 521 30811 9. FFT-smoothing should not be used in data files with spikes or discontinuities. It works best

if the noise only consists of a periodic disturbance with a higher frequency than the real signal. The real signal should not change much within one period of this periodic disturbance.
Please note that the presented frequency in the frequency domain plot is not the frequency of the noise in the current or potential signal. The frequency is presented in an arbitrary unit.

5.2 Change all points

This option allows to add a constant value to all data points or to multiply all datapoints with a constant value.

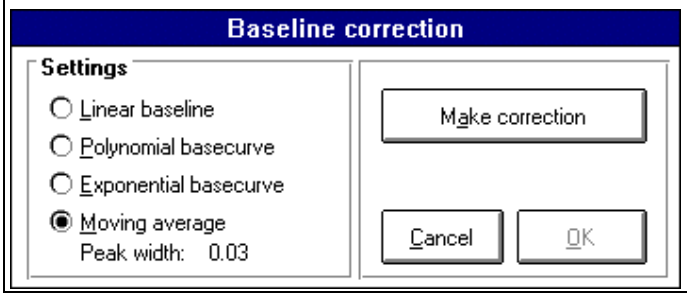
5.3 Delete points

It is possible to remove points from the plot. You can specify up to 20 points.
This option can be used to remove spikes from the measured data. With resume (Data presentation, Plot) the original data set will be loaded again. The Save work data (Data presentation, File) can be used to save the adjusted data-set.

5.4 Baseline correction

Four types of baselines can be specified.
The first is the linear baseline. Two markers on the measured curve can be specified, which then define a line. After acceptation of the markers, the corrected curve is also drawn. By clicking either the Cancel or the OK button on the Baseline correction window, the correction can be either ignored or accepted.
It is also possible to subtract a polynomial baseline. After selecting this option the user is asked to mark between two and five data points as contact points between baseline and curve. After accepting the markers the program will calculate a 3rd order polynomial through the markers.
The third type calculates a connecting exponential curve through the specified begin and end point. The whole curve is subsequently corrected for this baseline.
Finally, there is the so-called ‘Moving average baseline’. This is an automatic baseline correction. This method is very effective when peaks show as shoulders on steep flanks. After a baseline correction real peaks will show. The number of data points is reduced by calculating the average within a step window. The step window is the minimum peak width which can be specified on the Baseline correction window. The baseline is subsequently calculated by comparing each point with the mean value of its two neighbours. If the absolute mean value is lower, it replaces the current value. This operation is repeated again and again until no data point is replaced anymore. If more than 1000 iterations are required, a message is given and the process stops. As a default minimum peakwidth a value of 30 mV or less is advised in most cases. The process can be hindered by anomalies in the voltammogram. Please note that this technique cannot be applied for Cyclic and Linear sweep voltammograms.

Fig 52b: *Baseline correction window*



5.5 Subtract disk file

This option allows to subtract a previously measured data set from the current one. In case the spacing between the two data sets is different a linear interpolation method is used.

5.6 Subtraction of second signal from first signal.

This option allows to subtract a simultaneously measured second signal using either of the free ADC-channels from the current or potential signal (first signal). In case the spacing between the two data sets is different a linear interpolation method is used. The option is only enabled when a second signal is really available.

5.7 Derivative

First the data points are smoothed according to the Savitsky-Golay algorithm (see above) using smooth factor 2. Subsequently the derivative is determined by the simple algorithm:

$$dy/dx\,(n) = 0.5 * \left[\frac{y(n) - y(n-1)}{x(n) - x(n-1)}\right] + 0.5 * \left[\frac{y(n+1) - y(n)}{x(n+1) - x(n)}\right]$$

For cyclic and linear voltammetry the time derivative is given, i.e. x is the time since the start of the scan instead of the potential.

5.8 Integrate

The integral is determined using the trapezium rule, which assumes a straight line between two data points.

For cyclic and linear voltammetry the time integral is given, i.e. x is the time since the start of the scan instead of the potential.

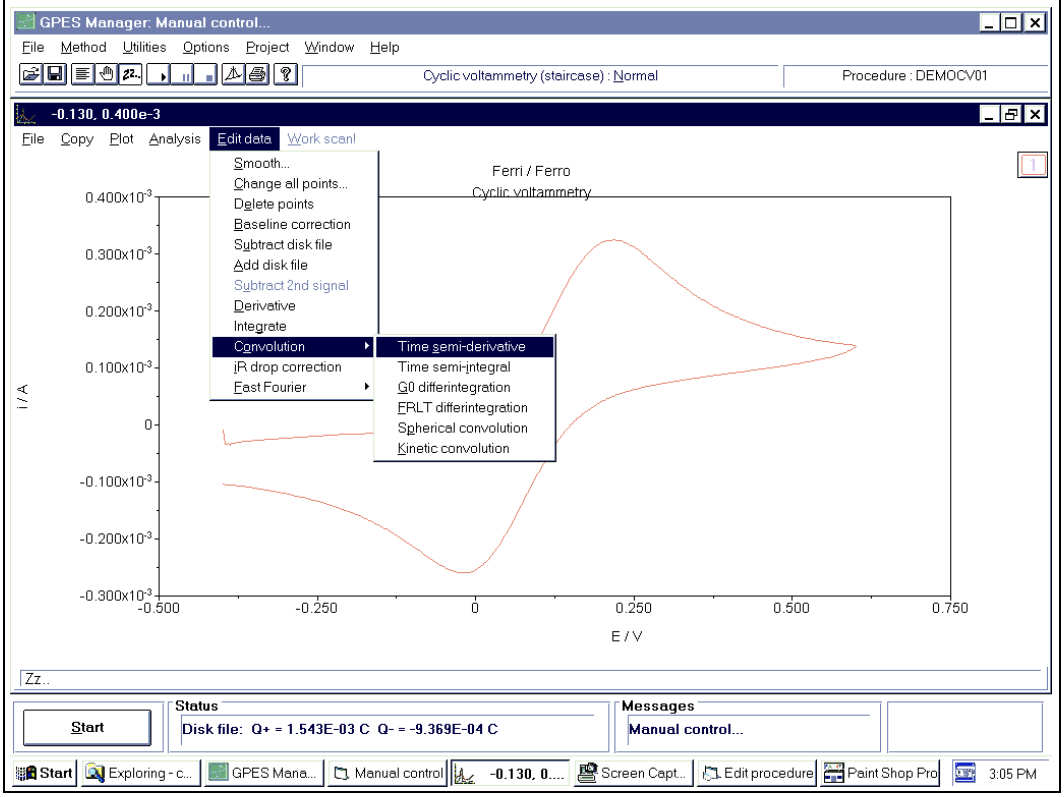
5.9 Fourier transform

The frequency spectrum is determined by means of a Fast Fourier method (FFT). The real frequency is displayed on the x-axis.

5.10 Convolution techniques

Convolution voltammetry consists essentially of a voltammetric, chronoamperometric, or chronocoulometric experiment followed by a mathematical transformation - convolution. The technique delivers quantities directly related to the concentration of electroactive species at the electrode surface (instead of the flux of a compound, as in the case of the original techniques) and it is rather insensitive to *iR*-drop.

Fig. 53 Convolution menu



In a number of electroanalytical techniques, the current measured displays proportionality to a $t^{-½}$ function. The popularity of this type of dependence originates from the solution of Fick's law in the case of semi-infinite linear diffusion, the most common type of the transport of the reagent to the electrode. According to this solution, the gradient of the concentration of a substance, consumed in the electrode process, decreases with the square root of the electrolysis time and so does the current which is proportional to this gradient. Such a dependence can be easily observed in chronocoulometry, chronoamperometry, and in voltammetry (in this latter case in the descending branch of the peak).

Using a convolution method, the effect of the decrease of the concentration gradient can be eliminated from the total response of the electrode. The surface concentration of the product of an electrode reaction during the experiment can be obtained using equation*.

$$c^s(t) = i(t)*g(t)/(nFAD^{½}) \qquad \text{(eq. 1)}$$

where $i(t)*g(t)$ is a convolution operation defined as

$$f_1(x)*f_2(x) = \int_0^x f_1(u)f_2(x-u)du = \int_0^x f_1(x-u)f_2(u)du \qquad \text{(eq. 2)}$$

The function $g(t)$ depends on the transport conditions and the electrode geometry, being in the simplest case $(\pi t)^{½}$. The convolution of a voltammogram results in an S-shaped curve, where voltammetric peaks are replaced by waves, very similar to polarographic ones. In the case of a fast and uncomplicated electron transfer, the wave can be described using the equation

$$E = E_{½} + (RT/nF)\ln[(m_d-m)/m] \qquad \text{(eq. 3)}$$

where m denotes current convolution (for approximate description of kinetic-controlled processes the RT/nF value should be replaced by $RT/\alpha nF$). The height of the plateau is given by the formula

$$m_d = nFAD^{½}C \qquad \text{(eq. 4)}$$

It can be shown that such a result is independent of the scan rate used and that the height of the wave is insensitive to *iR*-drop.
Convolution of voltammetric data with a $t^{-½}$ function results in a curve equivalent to the derivative of the previous one (up to a normalisation factor). Valuable features of this new curve can be noted: symmetric, narrow peaks which are much better resolved compared to asymmetric, "tailing" voltammetric ones. The obtained $t^{-½}$ convolution peak follows the function

*) K.B. Oldham, Anal. Chem. 58 (1986) 2296, J.C. Myland, K.B. Oldham, C.G. Zoski, J. Electroanal. Chem. 193 (1985) 3.

$$e = nFAD^{½}C\cosh^{-2}[nF/2RT(E-E°')] \qquad \text{(eq. 5)}$$

in case of a fast, reversible electron transfer.
It is also possible to use other convolution functions e.g. to separate the spherical diffusion effect, the kinetic effect of the preceding homogeneous reaction etc[*] .
In chronoamperometry, convolution of current with $t^{½}$ function results in a horizontal line at the height equal to

$$e = nFAD^{½}C \qquad \text{(eq. 6)}$$

if the transport to the electrode follows semi-infinite linear diffusion. For chronocoulometry, convolution with a $t^{-½}$function leads exactly to the same result.
It is profitable to distinguish a class of convolutions with a g(t) function in the form g(t)=t^{-u} (u is a real number): such a convolution can be considered as a generalised differentiation/integration (differintegration) operation with respect to the variable t. In this approach, the value of the exponent denotes the order of integration (if positive) or differentiation (if negative) and thanks to the convolution definition, the value of u need not be integer. Differintegration is cumulative, i.e. $d^{½}/dt^{½}$ ($d^{½}i/dt^{½}$) = di/dt or $d^{-½}/dt^{-½}$ (di/dt) = $d^{½}i/dt^{½}$. From the practical point of view, two forms of convolution, with $t^{½}$ and $t^{-½}$, deserve special attention. They can be considered as, respectively, semi-integration and semi-differentiation.
Another reason for mentioning differintegration is that there are special algorithms allowing this operation to be performed rapidly. For more information please refer to K.B. Oldham, J. Spanier, "The Fractional Calculus", Academic Press, N.Y., 1974.
As mentioned before, in case of semi-infinite linear diffusion the results of convolution with the function $t^{±½}$ (semi-integration and semi-differentiation) are well-defined and quite simple. This suggests that these methods can be used for the investigation of variations of product concentration on the electrode surface as well as detection and studies of phenomena, resulting in deviations from linear diffusion transport. Other practical applications are the resolution of overlapping voltammetric peaks, the determination of the formal potentials and numbers of electrons involved in the reaction step, detection of the adsorption on the electrode as well as of the irreversible homogeneous reaction consuming the product generated by the electron transfer step.

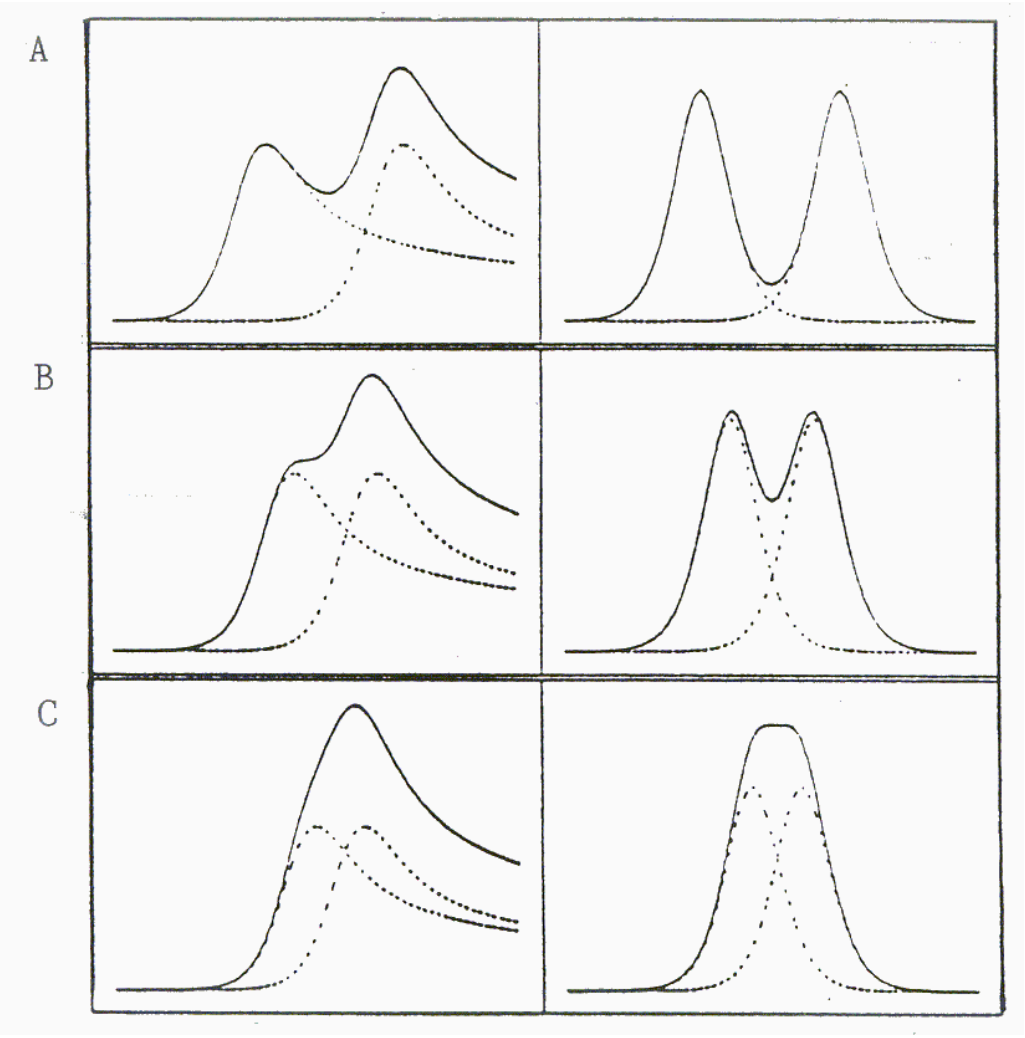
Detection of overlapping peaks

The nature of the voltammetric peak causes overlap in case of complex voltammograms. While the ascending branch of the peak rises rapidly and the beginning of the rise can easily be found, the descending branch follows a $t^{-½}$ function and is characterised with a slow decrease. Even far away from the top of the peak, the

[*]) F.E. Woodard, R.D. Goodin, P.J. Kinlen, Anal. Chem. 56 (1984) 1920, J.H. Carney, Anal. Chem. 47 (1975) 2267.

value of the current differs significantly from zero. Due to this feature, all following voltammetric peaks rise from the "tail" of the previous one.
If the separation of two voltammetric peaks is large enough, they can be detected without any problems. The situation is difficult when the distance between peaks gets smaller: below a certain distance, the first peak is reduced to a shoulder on the rising part of the next peak. The extreme situation is shown in fig. 56 C, where the overlap is very strong, so that only one peak can be observed and there is no indication for the presence of more of them.

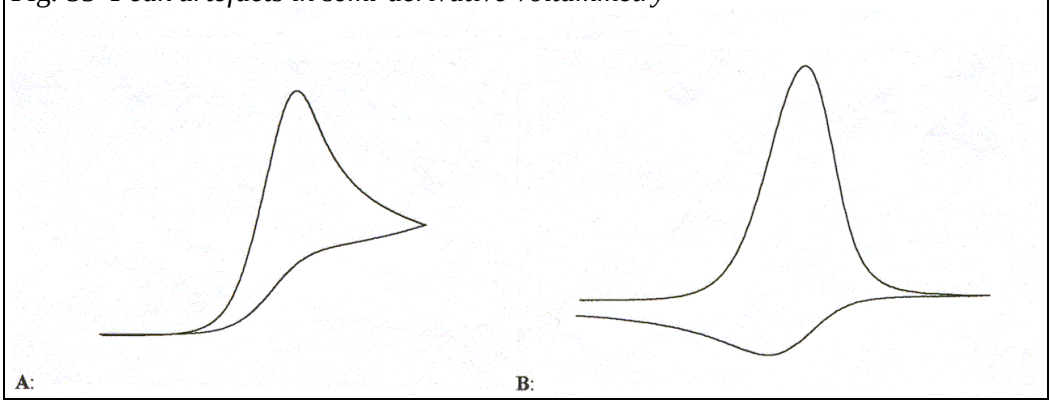
Fig. 54 *Overlapping linear voltammetric peaks and their semi-derivatives*



In most situations, except in those of extreme overlap, semi-derivative peaks are clearly visible and their number can easily be found. There are, however, three important limitations to this method. First, voltammograms that are to be semi-differentiated, should be background-corrected: semi-differentiation changes a constant or a linear background into complicated forms in the semi-derivative domain.

Secondly, semi-derivative peak artefacts have to be recognised: consider the case of an uncomplicated slow electron transfer leading to the voltammogram presented in the appropriate figure.

Fig. 55 *Peak artefacts in semi-derivative voltammetry*



The curve in the above-mentioned figure is the result of semi-differentiation, where two peaks appear, one in the forward and one in the backward branch. The second semi-derivative peak does not represent any hidden voltammetric peak, but is an artefact resulting from semi-differentiation of a wave-like current decay. Such a peak can only appear in the backward branch of semi-derivative voltammograms and has characteristic features: in the potential range, where such a peak appears, (i) there is no backward voltammetric peak, (ii) there is a forward peak and (iii) the sign of SCV current values is the same in both branches. All peaks that satisfy these criteria, are probably artefacts.
The third limitation of the method stems from the fact that results presented in the above-mentioned figure concern an uncomplicated electron transfer under semi-infinite linear diffusion conditions. The form of the peak is different when the mechanism of the reaction and the transport type change: usually peaks become less symmetric and broader, resulting in a decrease in separation capability and, in certain situations, leading to deformations of neighbouring semi-derivative peaks.

Determination of formal potential and the number of electrons involved

The equation 5 describes the form of a semi-derivative voltammetric peak in a case of uncomplicated fast electron transfer under semi-infinite linear diffusion transport. It is clear that the peak potential is equal to the formal potential of the reacting system and, for cyclic voltammetry, that both anodic and cathodic peaks appear at the same potential. This feature can be used as a simple and rapid test for reversibility of the reaction. This test is superior to the well-known test based on the difference of potentials of voltammetric peaks, as it does not require knowledge about the number of electrons involved.
If the rate of electrode reaction is limited by the diffusion or by kinetics of the electron transfer, the number of electrons involved can be determined from the half-width of the semi-derivative peak. This half-width should be

$$w = 3.53RT/nF \qquad \text{(eq. 7)}$$

for a diffusion-controlled process and

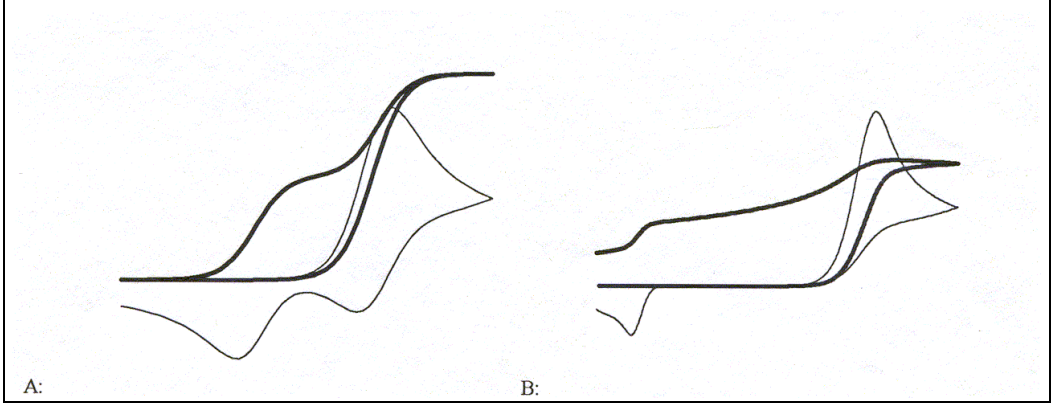
$$w = 2.94RT/\alpha nF \qquad \text{(eq. 8)}$$

for a rate-controlled process.

Irreversible homogeneous reaction consuming the product of the electrode process

The criterion for the absence of an irreversible homogeneous reaction is restoration of the initial state at the electrode surface after a cyclic change of electrode potential. If such a reaction does not occur, the surface concentration of all species after the experiment should be exactly the same as before.

Fig. 56 *Semi-integration of voltammograms in case of the absence (A) and the presence (B) of an irreversible homogenous reaction. Thin line - voltammogram, thick line - semi-integral*



As the convolution of the voltammetric current with a $t^{½}$ function (semi-integration) produces a value proportional to the surface concentration of the product of the reaction, the convoluted value should return exactly to zero after completion of the cycle, which means that the product of the reaction has been entirely converted back to the substrate*. If it does not return to zero, the consumption of the initially present substance is suggested.
It should be stressed, however, that this method requires diffusion to be semi-infinite and linear. In situations where this is not the case, corrections have to be made. Such a correction is available (S.O. Engblom, K.B. Oldham, Anal. Chem. 62(1990)625) for

*) F.E. Woodard, R.D. Goodin, P.J. Kinlen, Anal. Chem. 56 (1984) 1920, I.D. Dobson, N. Taylor, L.R.H. Tipping in "Electrochemistry, Sensors and Analysis" (M.R. Smyth, J.G. Vos, eds.), Elsevier, Amsterdam, 1986.

spherical electrodes (mercury drops) under the name of spherical convolution it requires the values of electrode radius and of diffusion coefficient, delivering the concentration of the reaction product on the surface of a spherical electrode.
If the presence of an irreversible homogeneous reaction is detected, its rate can be measured. For this purpose a so-called kinetic convolution can be used. In this transformation the effect of consumption of the product by the reaction with the rate *k* can be eliminated; by means of inserting different values of *k* one can obtain the result in which a convoluted current at the end of the cycle approaches the same value as on the beginning of the cycle.
Some problems can be expected if the substrate or the product of the reaction is accumulated on (or in) the electrode by adsorption, deposition, or amalgamation. In this case, the initial value of the surface concentration is not restored after the completion of the voltammetric cycle and convoluted voltammograms will not deliver proper results.

Investigations of factors controlling the transport to the electrode

Theoretically the most simple and quite commonly encountered transport type is semi-infinite linear diffusion: the substance diffuses from the bulk of the solution, where the concentration is constant, to the planar electrode, where it is consumed. The flux of the substance depends on the gradient of the concentration at the electrode surface; this gradient decreases with the rate proportional to the square root of the electrolysis time.
Linear diffusion leads to the simplest description, but unfortunately its conditions are rarely realised in the experimental setups used in electrochemistry. In case of mercury electrodes, the surface of the electrode is not planar, and the diffusion can be approximated using a linear model over a short period of time only. In case of solid electrodes a so-called edge effect occurs: the contribution of spherical diffusion appears. Apart from the geometry of electrodes, chemical processes taking place in the solution can disturb the concentration profiles developed during the electrolysis, for instance when electroactive species are produced by a homogeneous chemical process; another example of deviations from the linear model may be caused by the adsorption of the compound on the electrode surface.
It can be useful to consider different types of transport as deviations from the semi-infinite linear diffusion case. These deviations can then be classified into two groups: deviations, causing an increase of the transport to the electrode and those causing a decrease. In the first group, spherical diffusion and different kinetic effects are included; the second group covers effects such as limited diffusion and reaction from the adsorbed state.
Spherical diffusion enhances the transport because the spherical expansion of the diffusion zone increases its volume faster than in the semi-infinite linear case. The increased volume results in a larger amount of the substance that diffuses to the electrode.
Kinetic effects occur when the electroactive compound is involved in a chemical equilibrium. The local decrease of its concentration within the diffusion layer disturbs the equilibrium and in consequence leads to the production of the compound in a chemical process. This extra amount increases the flux of the substance to the electrode surface. Such conditions can be called mixed linear diffusion - kinetic effects. For a long electrolysis time, the kinetic increase of the flux can entirely

compensate the decrease of the concentration gradient and may lead to steady-state conditions provided that the amount of compound involved in reagent production is present in large excess.
Another type of effect can be observed when the solution is present in the form of a thin layer. Electrolysis under such circumstances first leads to the depletion of this layer and then to the exhaustion of the entire solution volume. This effect can relatively easily be observed in case of the dissolution of metals from a small amalgam drop or from amalgam film electrodes: the process is initially controlled by linear diffusion, but after some time the drop is depleted and the flux of the substance through the electrode surface drops more rapidly than $t^{-½}$. This is called limited diffusion.
An extreme case of this situation is the reaction of a substance adsorbed on the electrode or forming a monolayer on its surface. In such a case no transport is needed and the whole amount of substance reacts within a very short time. The measured current drops sharply to zero after exhaustion of the compound.

Cyclic chronoamperometry and chronocoulometry

If an electroactive compound reaches the electrode by means of semi-infinite linear diffusion, and the potential of the electrode is such that the surface concentration of the compound is kept zero, the current can be described using Cottrell's equation

$$i = nFAD^{½} C\pi^{-½} t^{-½} \qquad \text{(eq. 9)}$$

where n is the number of electrons involved, F - Faraday's constant, A - electrode area, D and C the diffusion coefficient and the bulk concentration of the compound, respectively, and t - time from the beginning of electrolysis. Integration of this equation leads to the expression for the charge

$$i = nFAD^{½} C\pi^{-½} t^{½} \qquad \text{(eq. 10)}$$

Semi-integration of eq. 9 or semi-differentiation of eq. 10 leads to the formula

$$m = nFAD^{½}C \qquad \text{(eq. 11)}$$

In case of additional contributions enhancing the transport due to, for instance, spherical diffusion or a kinetic effect, the semi-charge is greater than predicted from the purely linear model and the line displays positive bias. The inverse effect appears when the transport is slower than for limited diffusion or if the reagent is strongly adsorbed on the electrode.
There are a number of experimental problems, that should be mentioned here. First, the data used for studies of transport phenomena should be corrected for the background otherwise deviations from linearity of the graphs can have other reasons. In case of kinetic control of the process, the time scale of the experiment also

determines the range of reaction rates and equilibrium constants that can be detected. The quantitative discussion of influences of different experimental factors on the convolution curve can be found in Goto M, Oldham KB, Anal. Chem. 46(1974)1522.

Linear and staircase voltammetry

The convolution techniques facilitate the interpretation of voltammograms, particularly the information included in the peak shape. As already said, this shape can be considered as produced by the convolution of two functions: function I, describing the surface concentration of the reaction product, and function II, representing the flux of the reaction substrate, depending on the geometry of the measuring system.
In the simplest case of semi-infinite linear diffusion and fast electron transfer, function I has the form of an S-shaped wave and function II is a $t^{-½}$ decay. The character of function I is well-reflected in the ascending branch of the voltammetric peak; function II is responsible for the $t^{-½}$ - proportional decay of the descending branch of the peak. Semi-integration (convolution of the SCV peak with a $t^{½}$ function) should therefore give a wave with a horizontal plateau.
When the transport to the electrode is enhanced or diminished compared to semi-infinite linear diffusion, the descending branch of the SCV peak can be approximated using a t^{u} function, where $u>-0.5$ for faster transport (slower decay) and $u<-0.5$ for slower transport (faster decay). Changes in transport result in semi-integrated waves with a biased plateau (negative for slower transport, positive for a faster one).

Algorithms for convolution

As mentioned before, there are special algorithms for differintegration as well as for other convolution. Below, four algorithms used for differintegration and convolution are described in short.

G0 algorithm (Grünwald-0)

This algorithm can be used to carry out differintegration to any order. The data must be acquired in constant intervals. For the order = 1 the operation is equivalent to differentiation, for -1 - to integration using rectangle method. For +½ the G0 algorithm is the same as semi-differentiation. For -½ the G0 algorithm is the same as semi-integration. Error in results increases with the length of the interval and accumulates, i.e. error in latter points is larger than in earlier ones. Important advantage is that this algorithm does not require the value of the function for $t=0$, which makes it very well suited for transformation of chronoamperometric data (where $i(t=0)->\infty$. The disadvantage of the algorithm is that the total number of operations is proportional to the square of the number of data points, so calculation time grows fast with the length of the data set. The fundamentals of this algorithm are described in Oldham KB, J. Electroanal. Chem. 121(1981) 431.

FRLT algorithm (Fast Riemann-Liouville Transform)

This is a fast, approximate algorithm based on a recursive digital filter. It is best suited for differintegration in the range of 0.0...-0.5 (up to semi-integration). It is less precise than G0 algorithm, but the number of operations is linearly related to the number of

data points. For details refer to Pajkossy T, Nyikos L, J. Electroanal. Chem. 179(1984) 65.

Spherical convolution

The algorithm is used to carry out convolution of the data measured using a spherical electrode and staircase potential waveform. Values of the diffusion coefficient, the electrode radius as well as the delay between begin of the potential step and the current sampling moment are necessary. The number of operations is proportional to the square of data points. Details of the algorithm can be found in S.O. Engblom, K.B. Oldham, Anal. Chem. 62(1990)625.

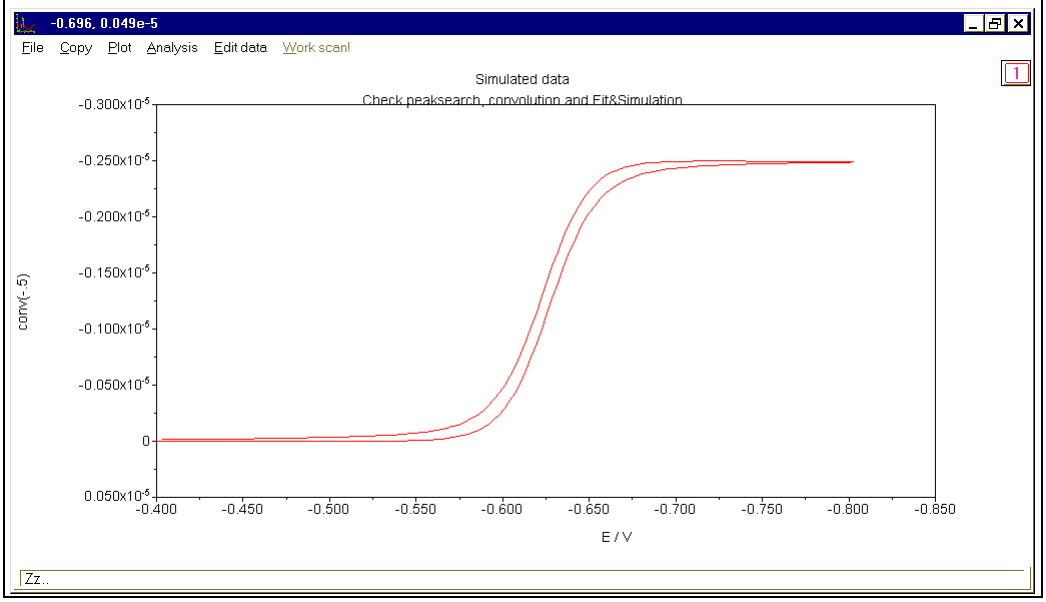
Kinetic convolution

This algorithm carries out kinetic convolution according to F.E. Woodard, R.D. Goodin, P.J. Kinlen, Anal. Chem. 56 (1984) 1920. The number of operations is approximately proportional to the square of the number of points. This convolution requires the value of the rate constant of irreversible homogeneous follow-up reaction (ECi mechanism).

5.11 Convolution in practice

The Convolution option can be selected for data measured with cyclic and linear sweep voltammetry. This convolution menu offers a number of transformations of the data set, like differentiation, integration, and convolutions.
There are three principal types of convolution available: differintegration (convolution with t^{-u} function, equivalent to fractional differentiation or integration, depending on u), using G0 or FRLT algorithm, spherical convolution, and kinetic convolution. The difference between G0 and FRLT algorithm is that G0 is more exact, while FRLT is faster with large data sets. Two items: semi-integration and semi-differentiation denote differintegrations using FRLT with the u value equal to -0.5 and 0.5, respectively.
It is possible to carry out more transformations in succession. Because differintegration is an operation that can be cumulated, double semi-differentiation is equivalent to differentiation and the integration followed by semi-differentiation is equal to semi-integration. Please note that some combinations, especially those involving differentiation are not equivalent: differentiation+integration is not the same as integration+differentiation.
In all convolutions the scale on the Y axis represents $c^s(t)nFAD^{½}$, where $c^s(t)$ is the concentration of the product of the electron transfer step on the surface of the electrode.

Fig. 57 *Example of a convoluted voltammogram*



It is also possible to perform the convolution on part of the voltammogram (See Set window option of the Plot menu).
It is recommended that the cyclic voltammogram starts at zero current. This can be achieved by performing a baseline correction.

5.12 iR drop correction

iR drop correction allows for software correction of the potential data for the Ohmic drop in the solution. This option can be used for data from cyclic and linear sweep voltammetry.
After supplying a value for the solution resistance, the measured and corrected curve are shown. The question appears whether the data are corrected.

Appendix I GPES data files

The following types of files are used by GPES

Graphical display settings for:

- cyclic and linear sweep voltammetry *.ici
- chronomethods *.ixi
- voltammetric analysis *.iei
- multi mode electrochemical detection *.idi
- potentiometric stripping analysis *.ipi
- steps and sweeps *.ifi
- electrochemical noise *.ini

These data files are in ASCII-format and are stored in the procedure directory and in the data directory.

Experiment parameter settings for:

- cyclic and linear sweep voltammetry *.icw
- chronomethods *.ixw
- voltammetric analysis *.iew
- multi mode electrochemical detection *.idw
- potentiometric stripping analysis *.ipw
- steps and sweeps *.ifw
- electrochemical noise *.inw

These data files are in ASCII-format and are stored in the procedure directory and in the data directory.

Measured data files for:

- cyclic and linear sweep voltammetry *.ocw
- chronomethods *.oxw
- voltammetric analysis *.oew
- multi mode electrochemical detection *.odw
- potentiometric stripping analysis *.opw
- steps and sweeps *.ofw
- electrochemical noise *.onw

These data files are in ASCII-format and are stored in the data directory.

Data memory buffer in binary format for:

- cyclic and linear sweep voltammetry *.bcw
- *.cv1
- *.cv2
- *.cv3

These data files are in binary format and are stored in the data directory.

Data memory buffer in ASCII-format and BAS Digisim file for:

- cyclic and linear sweep voltammetry *.txt

These data files are in ASCII-format and are stored in the data directory.

Project files containing command lines for automatic processing of measurement procedures and data analysis: *.mac
These data files are in ASCII format and are stored in the data directory.

Print template files: *.def
These data files are in ASCII format and are stored in the Autolab directory.

File containing anodic and cathodic charges in cyclic voltammetry: *.q&q
These data files are in ASCII format and are stored in the data directory.

The GPES executable file: gpes4.exe
The GPES binary help file: gpes40.hlp

The system parameter file, ASCII-format: sysdef40.inp
Description file of sysdef40.inp, ASCII-format: sysdef40.txt

Fit & simulation parameter files: *.efs

Appendix II definition of procedure parameters

CM : Chronomethods
CV : Cyclic and linear sweep voltammetry
ECD : Electrochemical detection
ECN : Electro Chemical Noise
PSA : Potentiometric stripping analysis
SAS : Steps and Sweeps
VA : Voltammetric analysis

ADC channel number: (Second signal, CV, CM)
The channel number which should be used for recording the output from an external source.

Amplitude: (VA ac voltammetry)
The root-mean-square value of the applied potential sine wave perturbation.
Amplitude: (VA square wave)
Half of the peak to peak value in the squared wave perturbation.

Base potential: (VA normal pulse, differential normal pulse)
The base potential level. The pulse will be superimposed on this potential level.

Begin potential: (CV linear sweep)
The potential at which the ramp starts.

Cell off after measurement: (All)
If not 'checked' the cell switch will be left in the 'on' position after the measurement procedure has been completed. The applied potential is the "stand-by potential".

Comment: (All)
A panel to type in several lines of text.

Conditioning potential: (VA)
This is the first potential applied after the start of the procedure. This potential is normally applied to clean the electrode surface. This potential is not applied when its duration is set to zero.

Correct iR-drop during dyn. iR: (CV, CM with dynamic iR compensation)
If ‘checked’ the potential will be corrected for the ohmic drop. If ‘not checked’ the value of the ohmic drop is determined only.

Current range: (bipotentiostat, CV, CM)
The input parameter only appears when the Autolab is equipped with the bipotentiostat module. The maximum range is 10 mA, the minimum range is 100 nA.

Cutoff on charge: (CM interval time > .1 s)
If checked, in chrono-amperometry or -coulometry, the specified cutoff value is charge, otherwise it is current. This feature allows to specify a cutoff value for the charge in chrono-amperometry.

Cutoff value: (CM interval time > .1 s)
If the specified value is exceeded, the measurements will proceed with the next potential level or, if it is the last potential level in the sequence, the measurements will stop.

Cutoff value for 2nd signal >(V'): (CV and CM interval time > .1s)
This value is the upper limit for the 2nd signal, as soon as this limit is reached, the experiment will stop.

Cutoff value for 2nd signal <(V'): (CV and CM interval time > .1s)
This value is the lower limit for the 2nd signal, as soon as the limit is reached, the experiment will stop.

Cutoff value for time >: (CM interval time > .1s)
The measurement is aborted when the time exceeds the specified value. It is only active when the option 'Specify time limit' is checked.

Define potential w.r.t. OCP: (CM)
If 'checked', the stand-by potential and the specified potential levels are applied with respect to the open circuit potential (OCP). Before the equilibration starts, the OCP is recorded. If sufficiently stationary, a button can be pressed to continue.

Define start potential w.r.t. OCP: (CV)
If this item is checked the measurement starts with measuring the OCP. After acceptance the Start potential will be corrected for the OCP (Start potential + OCP). If you want to start at the OCP.

Define vertex potential w.r.t. OCP: (CV)
If 'checked', the vertex and start potentials are specified with respect to the open circuit potential (OCP). Before the equilibration starts, the OCP is recorded. If sufficiently stationary, a button can be pressed to continue.

Deposition potential: (VA)
This is the second potential applied after the start of the procedure. This potential is normally applied to deposit the components to be analysed on the electrode. This potential is not applied when its duration is set to zero.

Direct output filename: (CM interval time > .1 s)
If a file name (without extension) is specified, the measured data are directly written to a data file with the extension ".oxw". This option may be useful for long duration measurements. It prevents loss of data due to a failure in the power supply.

If the number of measured data points exceeds the allowed maximum (default 10,000), the program will continue to store the data points on disk, although the data points are no longer plotted on the screen and stored in the computer memory. Also the data file becomes too long to be loaded by the GPES program.

Direct Output filename: (CV)
The path and the name of the file. The last five characters of the file name will be used as the scan number. This filename will be used for the Save every nth Cycle option.

Duration of Measurement: (ECN)
The total duration of the Measurement. It will be rounded to the next nearest power of 2 times the Interval time.

Dynamic iR amplitude: (CV, CM interval times > .1s)
The amplitude of the square wave in Dynamic iR compensation.

End potential[*] : (CV linear sweep, SAS)
The potential at which the ramp stops.

Equilibrate with potential pulses: (ECD)
If 'checked', the specified potential pulses are applied without recording data, otherwise the stand-by potential is applied.

Equilibration time: (All)
The time to equilibrate the electrode at the start potential (CV, VA) or the stand-by potential (CM, ECD, PSA).

Equilibration threshold level: (VA, CV, CM, ECD)
If enabled, the Equilibration stage will be aborted after reaching this specified current. The measurements will start as soon as this threshold value is exceeded. This option is not available for galvanostatic measurements.

Final rotation speed (rpm): (LSV staircase hydrodynamic)
The rotation speed applied during the last scan.

First conditioning potential[*] : (CV, CM, ECD)
The first potential which is applied after the Start button has been pressed. If the corresponding "Duration" is zero, the potential is not applied.

First potential boundary: (CV)
Used, in combination with ‘Second potential boundary’, for automatic calculation of the total positive and total negative charge. Only active when ‘Use boundaries for Q+/Q- calc.’ is ‘checked’.

---

[*]) In galvanostatic cyclic voltammetry or galvanostatic chronopotentiometry 'potential' should be read as 'current' and vice versa.

*First vertex potential** : (CV cyclic)
The potential goes from the start potential to the first vertex potential where it turns around to go to the second vertex potential.

Frequency: (VA)
The number of times the square wave or sine wave perturbation is applied per second in respectively square wave voltammetry and ac voltammetry.

Highest current range: (bipotentiostat, CV, CM)
The input parameter only appears when the Autolab is equipped with the bi-potentiostat module. The maximum range is 10 mA, the minimum range is 100 nA. The actual current range for the bi-potentiostat module will be automatically set between the specified 'highest' and 'lowest' current range.

Initial rotation speed (rpm): (LSV staircase hydrodynamic)
The rotation speed applied during the first scan.

Interval time: (CM interval time > .1 s)
Normally the time between two recorded data points. If a maximum dE, di, or dQ value is specified, the actual interval time can be less. For more information see the chapter on the methods.

Interval time: (ECD)
The time between two current measurements in dc-amperometry.

Interval time: (ECN)
The time between two recorded current and potential samples. It should be >= 0.002 s.

Interval time: (VA)
Time between two measurements.

Linear(1) or square root(2) distr.: (LSV staircase hydrodynamic)
The rotation speed table is calculated with a Linear distribution (1) or with a square root distribution (2). A linear distribution means that, when the initial speed is e.g. 100 and the final speed is e.g. 1000 with 10 scans, the subsequent rotation speeds will be 100, 200, 300, ... 1000.

*Lowest current range: (*bipotentiostat, CV, CM)
The input parameter only appears when the Autolab is equipped with the bi-potentiostat module. The maximum range is 10 mA, the minimum range is 100 nA. The actual current range for the bi-potentiostat module will be automatically set between the specified 'highest' and 'lowest' current range.

Maximum dE, di, or dQ: (CM interval time > .1 s)
In case the box "Specify maximum dE, di, or dQ" is 'checked' and if the change in current, charge, or potential exceeds the specified value, a data point will be recorded.

Maximum time interval: (CV, stationary current)
After this period the current is supposed to be stationary.

Maximum time of measurements: (PSA)
The measurements will stop when duration of the measurement exceeds the specified time.

Measurement temperature: (CV, CM with pH as second signal)
Temperature for pH correction with respect to the calibration temperature.

Minimum abs(di/i) per second: (CV, stationary current)
Every second the relative current change is determined. If during three seconds this relative change is less than the specified value the current is supposed to be stationary. The next potential is applied.

Minimum abs(di) per second: (CV, stationary current)
Every second the absolute current change is determined. If during three seconds this relative change is less than the specified value the current is supposed to be stationary.

Minimum variation: (CM)
Value at which the experiment is stopped or the next step in the experiment will be applied. This value is only active if the 'Specify minimum variation' is 'checked'.

Modulation amplitude: (VA differential pulse)
The height of the potential pulse. The pulse direction is the same as the scan direction when the specified amplitude is positive. If a negative amplitude is specified, the pulse direction is reversed with respect to the scan direction.

Modulation amplitude: (VA differential normal pulse)
Potential superimposed on the sum of base potential and pulse amplitude.

Modulation time: (VA)
Time during which the modulation amplitude(differential pulse, differential normal pulse) or the sine wave(ac voltammetry) is applied. A convenient value is 0.07 s for differential pulse and differential normal pulse. For ac-voltammetry 0.5 s is convenient.

Number of cycles: (CM interval times < .1 s)
The number of times the sequence of potential levels as specified in the potential level table are applied. After the measurements only the last cycle is in the computer memory. All the measured data of the previous cycles are lost. In most cases the number of cycles will be one, but for e.g. pulse plating experiments a higher number can be specified.

Number of cycles: (CM interval times > .1 s)
The number of cycles you want to measure. A cycle includes the pre-treatment. The old data (previous scan) will be overwritten by the new one. The direct output file (when specified) is appended with every scan. The time parameter also adds up.

Between two scans the interval time is recorded by the computer clock and this time is also added to the time parameter. After reaching the maximum number of points in memory (=10000) the on-line plot option will stop. The actual data-points however, will be in memory and are plotted after the ‘number of cycles’ has been reached or after pressing ‘Abort’.

Number of equilibration scans: (CV Scan averaging)
Number of cycles of linear sweeps to reach an equilibrium. The averaging starts after the specified number of scans. The equilibration scans are not kept in memory.

Number of potential steps: (CM)
During the measurements the potential steps from the stand-by potential to a number of potential levels. These levels can be specified under header 'Potentials'

Number of pulses: (ECD)
The number potential levels which should be applied in multiple pulse or differential pulse mode.

Number of scans: (CV)
The number of cycles or linear sweeps to be measured.
Number of scans: (LSV staircase hydrodynamic)
The number of scans with a different rotation speed.
Number of scans: (VA)
The number of times a voltammogram is recorded. The presented voltammogram is the average of all recorded voltammograms.

Phase: (VA ac voltammetry)
If "Phase sensitive" field above is ‘checked’, the supplied value will be the phase shift with respect to the applied ac potential at which the ac current is obtained.

Phase sensitive: (VA ac voltammetry)
If 'checked' a value for the phase should be supplied.

Potential: (bipotentiostat, CV, CM)
The input parameter only appears when the Autolab is equipped with the bipotentiostat module. The constant potential which should be applied to the second working electrode.

Potential limit: (PSA)
The measurements will stop when the potential passes the specified potential limit.

Potential shift: (CV)
The specified amount will be added to the recorded potentials of the voltammogram. In this way it is possible to record potential versus present reference electrode, but display them with respect to another.

Potentials[*] : (CM)
A table of potential levels can be specified. The number of rows is equal to the ‘number of potential levels’ specified on the field above. During a measurement sequence, the potential steps from the stand-by potential to each of the specified levels, The following columns can be specified in the potential table:
Potential: the required potential level
Duration: the time the potential level is applied
Sample time: the time between two current samples. This column is only present for the chronomethod with interval times < .1s. See description of the methods.

Potentials table: (ECD)
In this table the potential levels to be applied, and their duration can be specified in multiple pulse or differential pulse mode. The number of rows is equal to the "Number of pulses". In multiple pulse mode, in a third column, it can be specified whether the current should be recorded or not. In differential pulse mode the two levels, specified on page 2, are recorded.

Pulse time: (VA Normal pulse)
Time during which the potential pulse is applied.

Purge time: (All)
The time the gas valve is positioned to flow the gas through the cell. This parameter only appears when an automatic electrode is present (see Hardware configuration program).

Quick save of previous scan: (CV)
When more then one scan is recorded in Cyclic voltammetry, it is possible to save the previously measured scan. This option can also be activated by typing 'SAVE' on the keyboard. The path and the name of the file can be specified as the ‘Direct output filename’. The last five characters of the file name will be used as the scan number.

Record Bipotentiostat signal: (bipotentiostat, CV, CM)
The input parameter only appears when the Autolab is equipped with the bipotentiostat module.

Record second signal: (CV, CM)
The primary signal, current or potential, is sampled via one of the channels of the ADC164 or ADC124 analog to digital converter module.
If "Record second signal" is 'checked', the voltage level of an additional channel of the ADC164 or ADC124 module is sampled as well. The channel number can be specified.
The ADC164 or ADC124 module has 16 input channels which can be recorded. An internal multiplexer allows switching from one channel to another. Four of them have an external BNC-plug. Normally, input number three and four are free channels, i.e. not used by GPES. They can be used to record the output of another instrument.

---

[*]) In galvanostatic cyclic voltammetry or galvanostatic chronopotentiometry 'potential' should be read as 'current' and vice versa.

The input parameters, related to the second signal, do not appear when the Autolab is equipped with a bipotentiostat module.

Reverse scan for i> : (CV)
If "Specify current boundaries" is 'checked', the scan direction will be reversed if the current exceeds the specified value.

Reverse scan for i< : (CV)
If "Specify current boundaries" is 'checked', the scan direction will be reversed if the current becomes lower than the specified value.

Run time: (ECD)
The duration of the measurement.

Save every nth Cycle: (CV)
When more then one scan is to be recorded in Cyclic voltammetry, it is possible to save scan at regular intervals during the measurements. If this parameter is zero, no scans will be saved during the measurements, otherwise every nth scan will be stored on disk. If, e.g. '5' is specified, scan 1, 5, 10, 15 are saved. The path and the name of the file can be specified on page two of the Edit procedure window ('Direct output filename'). The last five characters of the file name will be used as the scan number.
Please note: These files can be overwritten during another measurement session with the same procedure.

Scan rate[*] : (CV Staircase)
The required speed of potential change. The lowest scan rate is 0.00001. The highest acceptable depends on the speed of the AD-converter, the computer, and the step potential. The essential number for the highest scan rate is the number of potential steps per second i.e. (scan rate)/(step potential). The maximum value is 4,800 with normal CV (2400 with Bipot or 2nd Signal). With Fast scan CV the maximum value is 45,000. The specified value is adjusted by the program, so that the number of steps per second becomes equal to one of the discrete values of the Autolab hardware timer. The maximum values might vary in combination with advanced options like “Specify current boundaries”, “High sensitivity”, “alpha (different from 1)” and “Chronoamperometry at vertexes”.

Scan rate: (CV Linear scan)
The required speed of potential change. The lowest scan rate is 0.001. This is a hardware limitation of the SCAN-GEN module.
The highest scan rate is 10,000 V/s for the SCAN-GEN module. As stated above, no more than about 4,800 samples per second can be taken in combination with the ADC164 or ADC124 module. This limits the measurable scan rate to about 10 V/s. Higher scan rates can be measured with ADC750 module, which allows to measure 750,000 samples per second.

Second conditioning potential[*]*:* (CV, CM, ECD)

---

[*]) In galvanostatic cyclic voltammetry or galvanostatic chronopotentiometry 'potential' should be read as 'current' and vice versa.

The second potential which is applied after the Start button has been pressed. If the corresponding "Duration" is zero, the potential is not applied.

Second potential boundary: (CV)
Used, in combination with ‘First potential boundary’, for automatic calculation of the total positive and total negative charge. Only active when ‘Use boundaries for Q+/Q- calc.’ is ‘checked’.

Second vertex potential: (CV cyclic)
The potential goes from the start potential to the first vertex potential where it turns around to go to the second vertex potential.

Show noise around zero Volt : (ECN, with ECN-module selected)
If ‘checked’ the potential noise will be plotted around zero volt in stead of around the DC-potential.

Signal multiplier: (Second signal, CV, CM)
The recorded "second signal" is measured in Volts. It can be multiplied by a factor to convert it into another unit.

Signal offset: (Second signal, CV, CM)
The recorded "second signal" is measured in Volts. An offset can be supplied to convert it into another unit.

Smooth level: (PSA)
The potential - time data are recorded. Subsequently the data are smoothed using the Savitsky-Golay algorithm and the derivative dt/dE is calculated.
See for further details the section on "smoothing".

Specify cutoff value for 2nd signal: (CV, CM interval times > .1s)
If ‘checked’, the 2nd signal will be checked on the ‘Cutoff value for 2nd signal >(V’)’ and ‘Cutoff value for 2nd signal <(V’)’. The measurement will stop (CV) or proceed with the next potential level or stop if it is the last potential level in the sequence (CM).

Specify current boundaries: (CV, normal, or stationary current mode)
If 'checked', the scan direction will be reversed, if the current exceeds one of the values specified below. In case of linear sweep voltammetry, the recording of the scan will be terminated.

Specify cutoff value: (CM interval time > .1s)
If 'checked' and the specified cutoff value is exceeded, the measurements will proceed with the next potential level or, if it is the last potential level in the sequence, the measurements will stop.

Specify maximum dE, di, or dQ: (CM interval time > .1s)
If 'checked', a data point will not only be recorded after the specified interval time, but also if the change in current, charge, or potential exceeds the specified value.

Specify minimum variation: (CM)
If ‘checked’, this parameter can be used to stop a chrono-amperometry or chrono-potentiometry experiment as soon as the change in, respectively, current or potential is less than the ‘Minimum variation’ value. In other words, as soon as the measured signal has reached the ‘Minimum variation’, the experiment is stopped or the next step in the experiment is applied.

Specify Time limit: (CM interval time > .1s)
If this option is checked, the measurement will stop when the time exceeds the value specified for ‘Cutoff value for time >’. This option might be of use when a large number of cycles is specified.

Stand-by potential[*] : (All)
The potential which is applied after the measurement in case of ‘cell on after measurement’. Sometimes (CM, ECD) it is also the 'start' potential before a measurement.

Start potential[*] : (CV, VA)
The potential at which the measurement, after the pre-treatment, begins.

Step potential[*] : (CV)
The potential increment between two successive current measurements. The specified value is adjusted by the program, so that it becomes equal to the closest 16 bit (DAC164) or 12 bit (DAC124) value and the number of steps per second becomes equal to the closest value of the Autolab hardware timer. See also "Scan rate".

[*]) In galvanostatic cyclic voltammetry or galvanostatic chronopotentiometry 'potential' should be read as 'current' and vice versa.

[*]) In galvanostatic cyclic voltammetry or galvanostatic chronopotentiometry 'potential' should be read as 'current' and vice versa.

Steps and sweeps table: (SAS)
A table in which up to 10 potential level or sweeps can be defined. The following items can be specified.
Segment type:

Not used	This level will not be included in the measurement
Step	One potential can be applied during a given time. The current is sampled with the specified interval time.
Staircase sweep	The potential sweeps from the previous applied potential to the End potential with the specified scan rate. The current is sampled at the end of every potential step. If the segment type of the first level is specified as a sweep, the start potential equals the Standby potential.
Linear sweep	Equal to Staircase sweep but performed with SCAN-GEN module. If the SCANGEN module is present, it is only possible to select Linear sweep segment (Staircase sweep is disabled).

Potential (V) (Step segment)

Sample time (s) (Step segment) (the lowest possible value is 0.0002 s)

Total time(s) (Step segment)

End potential (V) (Sweep segment)

Scan rate (V/s) (Sweep segment) (the highest possible value is 5000 times the step potential value)

Step potential (V) (Sweep segment)

The parameters for the Step segments are similar to the chrono-methods with short interval times (see items ‘Potentials’ in the appendix). The parameters for the Sweep segment are similar to the parameters for Linear sweep voltammetry.

Stirrer off during conditioning: (VA)
Switch off the stirrer of the Automatic electrode during the conditioning stage.

Stirrer off during deposition: (VA)
Switch off the stirrer of the Automatic electrode during the deposition stage.

Stop Equilibrium at threshold: (VA, CV, CM, ECD)
Enable the option to abort the equilibration stage when the Equilibration threshold level is reached.

Stop scan: (CV, linear sweep)
The recording of the sweep will be terminated if the current exceeds the upper or lower specified limit.

Surface area / cm^2: (CV & CM)
Surface area of the working electrode, with which the Current density can be calculated in the Analysis menu of the Data presentation window.

Switch cell off when i=0 A:(CM interval time < .1 s)
If this option is checked the cell will be switched off during levels specified with a current equals 0 A. This feature assures zero current. If this option is not checked, the current is set to zero with the cell switch 'on'. This means that a small offset current of maximum 0.2% of the selected current range can flow.

Tafel plot: (CV)
If checked, the x-axis becomes the 10Log-axis of the measured current and the y-axis becomes the potential axis. This option has been added to allow presentation of traditional Tafel plots. It does not give any functional contribution. Unless required, it is recommended to use this option. Normally recorded voltammograms can always be converted to corrosion plots:
Load previously measured data; check corrosion plot; save the data again; reload the data. Now the data should be presented as a corrosion plot.

Third conditioning potential[*] : (CV, CM, ECD)
The third potential which is applied after the Start button has been clicked. If the corresponding "Duration" is zero, the potential is not applied.

Time to wait for OCP: (CV, CM)
The time you want to wait for acceptance of the Open Circuit Potential. If this time has expired the program will continue using the OCP measured at that time. If this parameter is 0(zero), the program will not continue unless the 'Accept' button is pressed. If 0(zero) is specified in a procedure that is used in a project, the program will wait for 2 seconds at the OCP and will use the OCP measured at that moment.

Title and subtitle: (All)
Text lines to describe the experiment.
These lines are the same as the ones displayed above the plot.

Type of signal: (CV, CM)

Aux signal	-	Signal measured on selected ADC-channel
Charge	-	Calculated charge
Potential	-	Measured potential
Current	-	Measured current
ESPR	-	Measured response from ESPR device
pH	-	Measured response of the pX module (converted to pH, see Utilities menu, Calibrate pH-electrode)
pX	-	Measured response of the pX module

[*]) In galvanostatic cyclic voltammetry or galvanostatic chronopotentiometry 'potential' should be read as 'current' and vice versa.

Use ADC750: (CV, CM)
When the ADC750 module for fast AD conversions is present in the Autolab instrument, it can be used for fast CV or chrono measurements if an interval time is smaller than 100 µs.

Use boundaries for Q+/Q- calc.: (CV)
If 'checked' this option enables the user to set potential boundaries for automatic charge calculation. Between the first and second potential boundary the total positive and total negative charge will be calculated automatically. Charge values are displayed in the status bar, at the bottom of the screen. The option is mainly used for Cyclic Voltammetric Stripping in electroplating research. If this option is not checked, the 'First and Second vertex potential' are used as potential boundaries.

Use dynamic iR-compensation : (CV, CM interval times > .1s)
This options offers the possibility to measure and compensate for the Ohmic Drop during the measurement. This is useful in systems where the Ohmic Drop changes during the experiment. At every potential level, either a step in staircase cyclic voltammetry or a step in chronoamperometry, a small amplitude (Dynamic iR amplitude) high frequency square wave signal is added. By measuring the resulting current responses, the Ohmic Drop is calculated.
Please keep in mind that the following limitations apply to this technique:

- The sweep rate in cyclic voltammetry is limited.
- The method cannot be used in combination with a Rotating Disk Electrode, an ARRAY, ADC750, BIPOT, pX or ECD module or any other device (EQCM, ESPR, etc.) that will result in an external signal.
- Hardware adjustments are necessary for this option, so the option cannot be used on an older instrument with new software only.
- The method only works in High Speed mode.

Use ECN module: (ECN)
Use the ECN module to perform the noise measurements.

Use high ADC resolution:(CV staircase fast scan)
Fast scan measurements are done at a fixed gain. If this option is checked the measurement are done at gain 10 of the ADC-module, otherwise gain 1 is used.

Use lowest possible interval time: (CM interval times < .1s)
If this option is checked, the sample time per level will disappear from the table at page one. It is not possible to specify a sample time anymore. The sample time is calculated just after the measurement and depends on the speed of the PC that is used and on the type of AD converter included in the Autolab system. In general it is possible to get an interval time of approximately 19 µs.

Value of alpha: (CV staircase)
Fraction of the time interval, between two potential steps, at which the current is sampled. It should normally be 1. Only in cases where linear sweep voltammetry should be compared with staircase voltammetry, this number should be different. The number should be at least 0.25. Linear sweep voltammetry equals staircase voltammetry for reversible systems when $\alpha = 0.25$.
Ref.: M. Saralthan, R.A. Osteryoung, J. Electroanal. Chem. 222, 69 (1987).

Wait after first vertex: (CV, staircase cyclic voltammetry, normal or stationary current mode)
If 'checked', scanning will stop at the first vertex potential and a chronoamperogram will be recorded, with duration and sample time as specified. The chronoamperogram is not displayed on the screen, but the data are stored in memory and can be saved on disk using the File option on the Data presentation window.

Wait after second vertex: (CV, staircase cyclic voltammetry, normal or stationary current mode)
If 'checked', scanning will stop at the second vertex potential and a chronoamperogram will be recorded, with duration and sample time as specified. The chronoamperogram is not displayed on the screen, but the data are stored in memory and can be saved on disk using the File option on the Data presentation window.

Appendix III Combination of GPES and FRA

The FRA and GPES programs can be used at the same time. Moreover a FRA project file can be executed from GPES. The command FRA!Start(<"filename">) is available for this purpose.
However, in general it is important to note that both programs share the Autolab instrument and the graphics part of the software. Moreover, both programs require a considerable amount of the system resources. This means that when both programs are active, hardly any system resources are left. The amount of free system resources can be seen in option ‘About program manager’ in the Help menu of the Program manager window.

Practical rules are:

- The computer should be equipped with at least 32 MB RAM
- It is not possible that both programs are measuring and controlling the Autolab instrument
- Before the FRA program starts measuring, the ‘sleep mode’ in GPES is automatically switched on. This means that the GPES screen is no longer updated.
- Do not use function keys when both programs are active, because they will cause actions in both programs.
- When a measurement procedure is being executed, user interaction with the programs should be avoided.
- Apart from GPES and FRA no other program/window should be active.

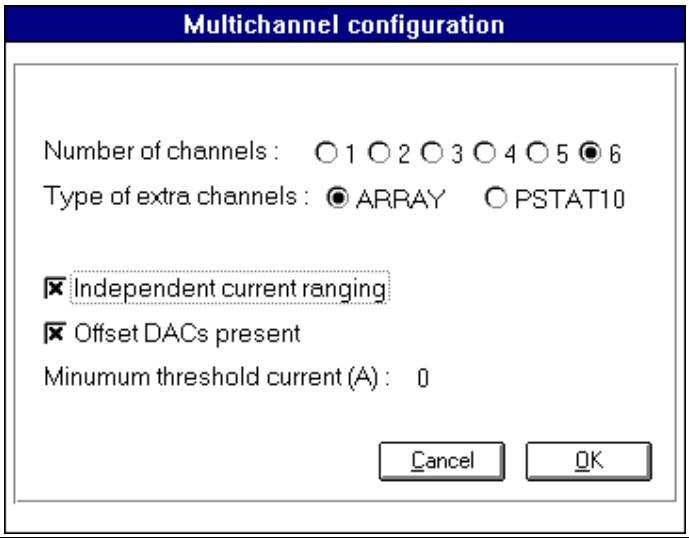
Appendix IV Multichannel control

It is possible to control the multichannel potentiostat with GPES. Activate the multichannel option by starting GPES with the shortcut "Multichannel GPES". The multichannel software is similar to the GPES software, however, some options are different or not available. The differences are explained in this paragraph.

Installation and test

The Hardware Setup program contains a button for Multichannel setup. After pressing this button the following screen appears:

Fig. 59 *Multichannel configuration*

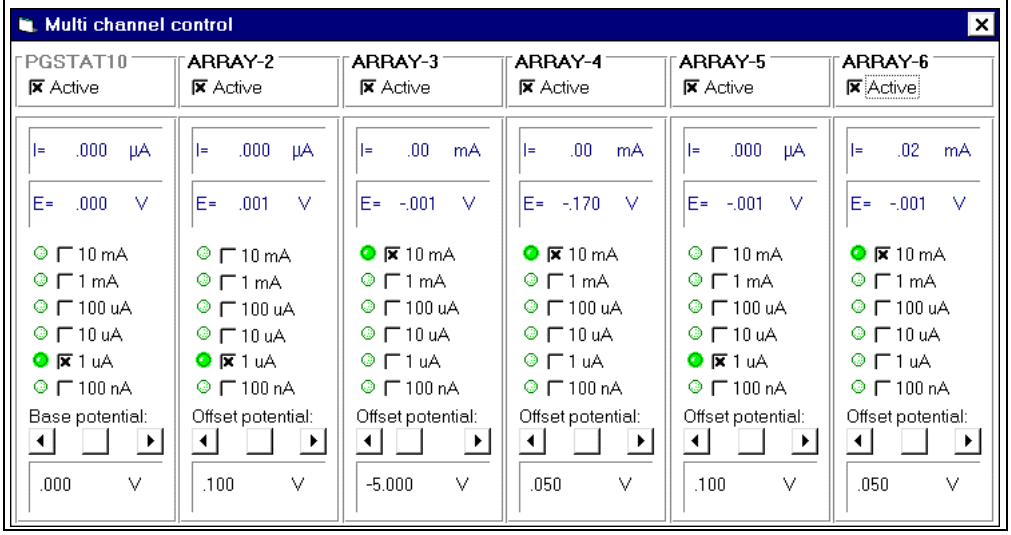

Multichannel configuration
Number of channels : 1 2 3 4 5 6
Type of extra channels : ARRAY PSTAT10
Independent current ranging
Offset DACs present
Minumum threshold current (A) : 0
Cancel
OK

The items above are factory settings and should normally not be changed. The test of the software is similar to the test of GPES. The procedure TESTCV6 can be used for more than one potentiostat.
If the multichannel system is equipped with ARRAY modules, one dummy cell is available. After loading the procedure TESTCV6 from the \AUTOLAB\TESTDATA-directory, the Multi channel control window shows that PGSTAT and ARRAY-2 are “active”. Now connect the dummy cell. The lead from ARRAY-2 should be connected to WE(b). After starting the execution of the procedure, the normal dummy cell response should appear and the current response should be the same for both channels. In a subsequent measurement ARRAY-3 can be connected to the dummy cell in stead of ARRAY-2. After ARRAY-2 has been made inactive and ARRAY-3 active, the same current response is expected. In this way all channels can be checked.
In case of a multi-PGSTAT10 set-up two dummy cells should be available. The PGSTAT10-2 should be connected to the second dummy cell. Then the same procedure should be followed as for the multi-ARRAY set-up as described above.
The DIAGNOST test is available, but does not work properly. The “zero-test” of the ADC does not work properly because the test-channel is used for one of the extra channels.

Program operation

After starting the program an extra Window appears :

Fig. 60 *Multi channel control window*



When this window is behind other windows on the screen it can be shown with the Window option from the GPES manager. The last item is Multichannel. After clicking this item the multichannel window will be shown. Depending on the configuration, this screen will be adjusted. The base potential for all arrays, including the PGSTAT, can be set in the PGSTAT panel. If offset DAC's are present, a specified offset potential can be given.
With 'Dependent current ranging' the current range of all channels will be the same. Changing the current range of 'Array 4' will lead to a current range change of all channels. The Active-option button allows to select the channels that should be measured. Note that the potential will always be applied to all channels.
The number of items on the Manual control window is considerably reduced compared to normal GPES.
On the Data presentation window two additional items are present.

1. The Signal menu allows to select the signal from which channel is the active work signal. All Edit and Analysis operation will be performed on this signal. The currently selected signal is shown between brackets.
2. The Plot overlay signal option in the Plot menu allows to overlay several signals. It operates similarly to the other overlay options.

The following methods are available in the multichannel mode:

Voltammetric analysis

- Differential pulse
- Square wave
- Sampled DC
- Normal pulse

Cyclic voltammetry
- Normal

Linear sweep voltammetry
- Normal

Chronomethods
- Amperometry
- Potentiometry

During the measurements, the sampling duration is the same as in the normal GPES. This is described in the chapter about the Methods. However in the multichannel mode all six possible channels sampled one after an other. So the number of samples per channel from which the average registered current c.q. potential value is, one sixth of the normal GPES. If a channel is specified as 'active', it only means that the measured current c.q. potential is registered.
The minimum sampling time is equal to 6 ranged AD-conversion and this is 6 times as long as in normal GPES. This has a consequence for the minimum interval time in Chronomethods with short interval times. The minimum time is now about 800 microseconds (see also the information about the manual control window).
Specifications of the instrument are almost similar to those of the PGSTAT10 potentiostat.

Appendix V Technical specifications

	µAutolab type III	**Autolab with PGSTAT12**	**Autolab with PGSTAT302N**	**Autolab with PGSTAT100**
maximum output current	± 80 mA	± 250 mA	± 2 A	± 250 mA
maximum output voltage	± 12 V	± 12 V	± 30 V	± 100 V
potentiostat	yes	yes	yes	yes
galvanostat	yes	yes	yes	yes
potential range	± 5 V	± 10 V	± 10 V	± 10 V
applied potential accuracy	± 0.2% of setting 2 mV	± 0.2% of setting 2 mV	± 0.2% of setting 2 mV	± 0.2% of setting 2 mV
applied potential resolution	150 µV	150 µV	150 µV	150 µV
measured potential resolution	300 or 30 µV	300 or 30 µV	300 or 30 µV	300 or 30 µV
current ranges	10 nA to 10 mA in seven ranges	10 nA to 100 mA in eight ranges	10 nA to 1 A in nine ranges	10 nA to 100 mA in eight ranges
applied and measured current accuracy	± 0.2% of current and ± 0.2% of current range	± 0.2% of current and ± 0.2% of current range	± 0.2% of current and ± 0.2% of current range	± 0.2% of current and ± 0.2% of current range
applied current resolution	0.015% of current range	0.015% of current range	0.015% of current range	0.015% of current range
measured current resolution	0.0003% of current range	0.0003% of current range	0.0003% of current range	0.0003% of current range
- at current range of 10 nA	30 fA	30 fA	30 fA	30 fA
potentiostat bandwidth (1)	500 kHz	500 kHz	>1 MHz	500 kHz
- potentiostat risetime/falltime (1 V step, 10-90%) (1)	1 µs	< 500 ns	< 250 ns (with external source)	< 500 ns
potentiostat modes	high speed/ high stability	high speed/ high stability	high speed/ high stability	high speed/ high stability
input impedance of electrometer	> 100 GΩ//< 8 pF	> 100 GΩ//< 8 pF	> 1 TΩ//< 8 pF	> 100 GΩ//< 8 pF
input bias current @25°C	< 1 pA	< 1 pA	< 1 pA	< 1 pA
bandwidth of electrometer	> 4 MHz	> 4 MHz	> 4 MHz	> 4 MHz
IR-compensation	n.a.	depending on selected range: 0Ω-200Ω at 100 mA range to 0Ω-200 MΩ at 10 nA range, current interrupt and positive feedback available	depending on selected range: 0Ω-20Ω at 1 A range to 0Ω-200 MΩ at 10 nA range, current interrupt and positive feedback available	depending on selected range: 0Ω-200Ω at 100 mA range to 0Ω-200 MΩ at 10 nA range, current interrupt and positive feedback available
- resolution	n.a.	0.025%	0.025%	0.025%
four electrode control	no	yes	yes	yes
front panel meter	no	potential and current	potential and current	potential and current
Analog outputs (BNC connector)	potential and current	potential, current and optionally charge	potential, current and optionally charge	potential, current and optionally charge
control voltage input	no	yes	yes	yes
multichannel option	no	multipleWE option	multipleWE option	no

	µAutolab type III	**Autolab with PGSTAT12**	**Autolab with PGSTAT302N**	**Autolab with PGSTAT100**
booster option	no	no	yes	on request BSTR10A only
analog integrator	yes	optionally available	optionally available	optionally available
- time constants	10 and 100 ms, 1 and 10 s	10 and 100 ms, 1 and 10 s	10 and 100 ms, 1 and 10 s	10 and 100 ms, 1 and 10 s
interfacing	USB	USB	USB	USB
A/D converter	16-bit with software programmable gains of 1, 10 and 100	16-bit with software programmable gains of 1, 10 and 100	16-bit with software programmable gains of 1, 10 and 100	16-bit with software programmable gains of 1, 10 and 100
auxiliary input channels	1	2	2	2
D/A converter	16-bit three channels	16-bit, four channels (optionally eight)	16-bit, four channels (optionally eight)	16-bit, four channels (optionally eight)
auxiliary output channel	1	1	1	1
digital I/O lines	48	48	48	48
(W x D x H)	26 x 26 x 10 cm³	52 x 42 x 17 cm³	51.5 x 41.6 x 16 cm³	52 x 42 x 17 cm³
weight	3.6 kg (4.2kg / FRA2)	18 kg	18 kg	21 kg
power requirements	144 W 100-240 V, 50/60 Hz	247 W 100-240 V, 50/60 Hz	247 W 100-240 V, 50/60 Hz	300 W 100-240 V, 50/60 Hz

Notes: (1) Measured at 1 mA current range, 1 kOhm impedance, high speed mode when applicable. All specifications at 25°C.

Interface for mercury electrodes (IME 303 and IME663)

Supported electrodes

- Metrohm VA Stand 663
- EG&G PAR303(A)
- dropping mercury electrodes with knock-off hammer

Control lines

- new drop
- purge on/off
- stirrer on/off

Burettes

- Metrohm Dosimat 665/765
- Schott T90 and T100

Hardware specifications of optional modules

SCAN-GEN, SCAN250: analog scan generator module

	SCAN-GEN	**SCAN250**
scan range	± 5 V relative to initial potential	± 5 V relative to initial potential
vertex potentials	2.5 mV resolution and 5 mV accuracy	2.5 mV resolution and 2 mV accuracy
output offset	± 1 mV maximum	± 0.2 mV maximum
ranges of scan rates	100 mV/s to 10 kV/s full scale (6 ranges)	100 mV/s to 10kV/s full scale (6 ranges)
scan rate - resolution	1 in 4096	1 in 4096
- accuracy	± (0.2% full scale+500 µV/s)	± (0.2% full scale+500 µV/s)
- temperature dependence	<0.04%/K	<0.04%/K
- minimum	100mV/s	100mV/s
- maximum	10kV/s	10kV/s
hold mode	available	available
maximum number of scans	32767	32767
monitor output (BNC)	scan signal	scan signal

ADC750: dual channel fast ADC module

• number of ADCs	2, each with four input channels
• maximum conversion rate	750 kHz
• maximum integration time	5.5 ms (mean of 4096 AD conversions)
• basic resolution	1 in 4096 (12 bit)
• resolution of measurements	- potential 5 mV at range 10 V 2 mV at range 4 V 1 mV at range 2 V
	- current 0.5%, 0.05% and 0.005% of full scale
• memory	128000 samples per channel (optionally 512000 samples)

ECD: low current amplifier module

• current ranges	100 pA to 100 µA full scale (seven ranges) 1 pA and 10 pA with selectable-gain amplifier
• current measurement	± 0.5% accuracy
• type of filter	third order Sallen-Key
• filter time constants	RC-times 0 s, 10 ms, 100 ms and 500 ms
• compensation of current offset	± 10 µA maximum
• monitor output (BNC)	current

BIPOT, ARRAY and BA: (bipotentiostat) module

	BIPOT/ARRAY	**BA**
current ranges	100 nA to 10 mA full scale (6 ranges)	10 nA to 10 mA full scale (7 ranges)
current measurement	± 0.2% of current ± 0.2% of current range	± 0.2% of current ± 0.2% of current range
maximum current output	± 35 mA	± 50 mA
potential range	± 5 V	± 10 V
potential accuracy	± (0.2% + 2 mV)	± (0.2% + 2 mV)
monitor output (BNC)	current	current

FI20: filter and integrator module

• filter section	
- type of filter	third order Sallen-Key
- filter time constants	RC-times 0 s, 10 ms, 100 ms and 500 ms
- output offset	± 2 mV
- monitor output (BNC)	filter output
• integrator section	
- ranges	10 ms, 100 ms, 1 s and 10 s
- charge measurement	0.2% accuracy
- temperature dependence	< 0.04%/K
- monitor output (BNC)	charge output

BSTR10A or Booster20A: current booster

	BSTR10A	**Booster20A**
maximum output voltage	± 20 V	± 20 V
maximum output current	± 10 A	± 20 A
maximum output power	200 W	400 W
bandwidth	4 kHz full power	20 kHz
current measurement	10 A full scale ± 0.5% accuracy	.1% of full scale = 20mA
dimensions (W x D x H)	37 x 36 x 15.5 cm^3	52 x 42 x 17 cm^3
weight	approx. 9 kg	approx. 25 kg

Note: Specifications subject to change without notice. All specifications at 25°C.

Index

A

ac voltammetry....113, 116, 117, 118
Analysis results....64
Automatic....59
axis annotation....58, 60

B

BAS-DigiSim....30
basecurve....67
baseline....44, 67, 68, 74, 98, 110
Batch mode....43
Burette control....34

C

Calibrate pH-Electrode....39
Check cell....40, 42
Chronoamperometric plot....69
chronoamperometry....100, 102, 107
Chronocoulometric plot....69
chronocoulometry....56, 100, 102, 107
chronomethods....7, 47, 63
colours....61, 63
Computer....5, 6, 115, 117, 120
configuration....5, 6, 42
convolution....108
Convolution....70, 100
Copy....43, 58, 64
corrosion....5, 71, 72, 73, 124
corrosion rate....19, 71, 72, 73
Coulometric titration....95
Crank-Nicolson....75
Current density....95
current range....37, 54, 55, 113
curve cursor....67
cyclic voltammetry....104, 126

D

Data buffer....31
Delete files....31
derivative....68, 69, 71, 99, 101, 103, 104, 121
differential pulse....64, 117
DIO ports....49
dt/dE vs E plot....59

E

E vs t plot....59

Edit procedure 32, 63
electrochemical detection 5, 47, 60
Electrode control 33
Enter text 60
Exit 31
Export Chrono data 30
Export data buffer 30
Export to BAS-DigiSim data 30

F

FFT 73, 97
Filter for derivative 96
First- and Second signal 59
Fit 74
free cursor 67, 68
frequency spectrum 73

G

galvanostat 5, 6, 30
GPES 3 files 28
GPES3 files 28
graphics 5, 6, 27, 63

H

help 5, 7, 52, 63, 112
High sensitivity 54

I

Idisk 95
I-interrupt 37
integrate 99
integrator 53, 56
Interpolate 74
iR drop 110
iR-compensation 37, 39, 55
Iring 95

L

linear regression 69, 70, 74
linear sweep voltammetry 29, 47, 63, 126
Load data 28, 31
Load scan 28

M

manual control 6, 37, 53
Marquardt 75
Mercury drop electrode 53
Method menu 32
Metrohm 730 Sample Changer 49
mouse 6, 28

MS-Windows 5, 6
MS-Word 6, 56, 58, 64
MULTI4 36
MUX control 36

N

New plot 58
noise 40, 42, 69, 97, 98
normal pulse 113, 119

O

Open procedure 27
overlay 60

P

peak search 60, 65, 67, 68
pH buffer 40
pH electrodes 39
Plate 42
plot title 61
polarisation resistance 71, 72
Positive feedback 38
potentiometric stripping analysis 59, 64
potentiostat 5, 6, 27, 38, 39
Print 6, 28, 112
Procedure name in Data presentation Window 52
Project 43, 112
Project command rules 43
Project examples 48
Project wizard 47
pX/pH 95

Q

Quick save 57

R

RDE-control 35
Rescale after measurement 52
Rescale during measurement 52
Resume 59, 60
Reverse axes 60

S

Save data 29, 30, 57
Save procedure 28
Save procedure as 28
Save scan 29
Scan averaging 118
SCNR16A 36
SCNR8A 36

second signal 55, 59, 65, 113, 119, 121
Set window 59, 110
Show all GPES files in File dialog box 52
Show I (backward) 59
Show I (forward) 59
simulation 74
Sleep mode 42
smooth 44, 97, 99
Smooth 121
Spectral noise analysis 73
square wave 113, 116
Start button 53
stationary current 117, 121, 126
Status bar 53
surface area 95

T

Tafel slope 70, 71, 72, 73
tool bar 6, 52
transition time 59, 74
trigger 49, 51

V

viewing data 60
voltammetric analysis 5, 63, 70

W

Wave log 16, 70
WE2 versus WE plot 95
Window for zero crossings 96
Window function 74
Work potential 60
Work scan 60, 65

Z

zoom 6, 59